Attorney Docket: 1321-14 PCT US

IN THE UNITED STATES RECEIVING OFFICE

Applicant(s): Yang, et al.   Examiner: Lee, Doris L.

Serial No.: 10/518,965   Group Art Unit: 1796

Filed: August 1, 2005

For: **A DURABLE FLAME RETARDANT FINISH
        FOR CELLULOSIC MATERIALS**

Mail Stop: RCE
Commissioner for Patents
P.O. Box 1450
Alexandria. VA 22313-1450

DECLARATION OF DR. JEFFREY K. STOWELL UNDER 37 C.F.R § 1.132

I, Dr. Jeffrey K. Stowell, declare and say as follows:

1.   I am one of the joint inventors of the invention being claimed in the above-identified patent application.

2.   I graduated from Illinois Wesleyan University in 1991 with a Bachelor of Science in chemistry. In 1996, I received a Ph.D in organic chemistry from Indiana University. While at Indiana University, I worked on the design and synthesis of novel mechanism-based enzyme inhibitors of phosphatases and phosphodiesterases for Professor Theodore Widlanski. That work resulted in several publications in prestigious journals such as the Journal of Organic Chemistry, Journal of the American Chemical Society, and Tetrahedron Letters.

3.   After completing my Ph.D. at Indiana University, I joined the Phosphorus Chemicals Division Akzo Nobel in 1996 as a Research Chemist in

charge of the synthesis, application, and process development of new phosphorus-based flame retardant additives. Over the past thirteen years, I have encountered and overcome many challenging obstacles in projects ranging from the synthesis of new molecules to the process and application development of both new and existing products. During my time working with Akzo Nobel, I have been promoted for my work several times (in 1998 to Senior Research Chemist, in 2001 to Principal Research Chemist, in 2007 to Scientist). Currently, I hold the title of Scientist and manage a small group of researchers. My current work is focused on the synthesis and development of new halogen-free flame retardant products for polyurethane foam applications. I hold a plurality of U.S. patents and have authored and co-authored many technical papers.

4. I have read and understand the Office Action mailed January 26, 2009 ("Office Action"), by the United States Patent and Trademark Office in the above-identified application and the art being applied therein, namely U.S. Pat. No. 3,639,096 to Wright ("Wright").

5. In the response mailed to the United States Patent and Trademark Office on December 18, 2008 to the previous Office Action, a Declaration was filed stating that one skilled in the art would not add hydroxyl-functional phosphorous esters containing at least two phosphorous atoms to the Wright invention since doing so would render Wright unsatisfactory for its intended purpose. In particular, as stated in the first Declaration, Wright teaches away from the addition of anything that would not result in a composition that will impart wrinkle resistant properties.

6. In the Office Action mailed January 26, 2009, the Examiner acknowledged the Declaration but stated that the "applicant speculates (see e.g. paragraphs 9-11 of the Declaration) that the introduction of Fearing's hydroxyl-functional phosphorus ester containing at least two phosphorous atoms would (undesirably) crosslink with hydroxyl groups present in Wright's cotton fabric

rather than promote a different kind of crosslinking reaction. . .).

7.   Given the Examiner's comment that there is no data to support the arguments made in the original Declaration, provided herewith are three literature citations that provide the necessary evidence and support for the arguments presented in the previous Declaration. The citations are as follows:

-    Citation #1: (See Exhibit A):

Yang C., Wu W., Xu Y. The combination of a hydroxy-functional organophosphorus oligomer and melamine-formaldehyde as a flame retarding finishing system for cotton: *Fire and Materials* 2005; **29**: 109–120

-    Citation #2: (See Exhibit B):

Yang C., Wu W. Comparison of DMDHEU and Melamine-formaldehyde as the Binding Agents for a Hydroxy-functional Organophosphorus Flame Retarding Agent on Cotton: *Journal of Fire Sciences* 2004; **22**: 125-142

-    Citation #3; (See Exhibit C):

Wu W., Yang C. Comparison of different reactive organophosphorus flame retardant agents for cotton: Part I. The bonding of the flame retardant agents to cotton: *Polymer Degradation and Stability* 2006; **91**: 2541-2548.

8.   As discussed in the previous declaration, the mechanism for chemical modification of cotton by melamine formaldehyde and DMDHEU type resins to produce a wrinkle-resistant (a.k.a. durable press finish) is well known in the literature. As described in Chapter 23 of The American Cotton Handbook,

wrinkle-resistant finishes are given their properties by the resin's ability to crosslink hydroxyl groups located on different parts of the cotton fibers.

9. The standard method for evaluating the wrinkle-resistant properties of a fabric is by measuring the conditioned wrinkle recovery angle (WRA) according to AATCC Standard Method 66-1996 in which test specimens are folded and compressed under controlled conditions of time and force to create a folded wrinkle. The test specimens are then suspended in a test instrument for a controlled recovery period, after which the recovery angle is recorded. An untreated fabric with low durable press qualities will have a WRA typically around 205°, while a fabric crosslinked with a resin binder will typically have much higher WRA around 300° depending on the type of quantity of resin used.

10. Since the durability of a hydroxyl-functional flame retardant is dependant on using that same resin molecule discussed above to crosslink it to a cotton hydroxyl group, the introduction of hydroxyl-functional flame retardant would significantly degrade the wrinkle resistant properties and resulting WRA values for a treated fabric. As shown in the three citations listed above, there are clear examples showing that the addition of a hydroxyl functional flame retardant such as that described in patent application would significantly deteriorate the WRA / wrinkle resistant properties of the durable press resin systems.

11. This trend is shown quite well in Figure 1 on page 112 of Citation #1 (See Exhibit A) in which the resin without FR shows an increasing

WRA as the level of resin is increased, while at the same time the system with FR shows very low wrinkle resistant properties at all resin levels. It is clear that there is very little cotton-resin-cotton crosslinking occurring in the system containing the FR. A conclusion stating this is present in the paragraph on the bottom of page 112 of Exhibit A.

11.   In addition, Citation #2 (See Exhibit B) shows similar data in Figures 1 and 2 (pages 129 and 131 respectively) for resin systems based on both DMDHEU and M-F. The introduction of FR to the durable press resin systems shown significantly reduces the wrinkle resistant properties of the systems by interfering with the normal cotton-resin-cotton crosslinking reaction. Similar data and conclusions are given in Citation #3 (See Exhibit C).

12.   With the additional information provided by these three specific citations, it is now clearly shown that the introduction of FR into Wright's formulation would render it unsatisfactory for its intended purpose by producing a resin system with significantly degraded wrinkle resistant properties.

13.   Accordingly, as one skilled in the art having reviewed Wright, I would not add a hydroxyl-functional phosphorus ester containing at least two phosphorous atoms therein to the finishing system in Wright since it would render Wright unsatisfactory for its intended purpose. Indeed, the addition of a hydroxyl-functional phosphorus ester containing at least two phosphorous atoms to the composition in Wright would cause the hydroxyl-functional phosphorus ester containing at least two phosphorous atoms therein to cross-link with cotton

hydroxyl groups, rather than promoting cross-linking between the melamine formaldehyde and DMDHEU to the hydroxyl groups on the cotton fabric hydroxyl groups located on different parts of the cotton fibers. In that wrinkle-resistant finishes are given their properties by promoting cross-linking between the melamine formaldehyde and DMDHEU to the hydroxyl groups on the cotton fabric hydroxyl groups located on different parts of the cotton fiber, adding a hydroxyl-functional phosphorus ester containing at least two phosphorous atoms therein would respectfully interfere with this arrangement and therefore not produce a finish possessing the desired wrinkle-resistant properties.

14. All statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further these statements are made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and such willful false statement may jeopardize the validity of the application or any patent issued thereon.

_5/20/09_
Date

Dr. Jeffrey K. Stowell

6

Exhibit A

The combination of a hydroxy-functional organophosphorus oligomer and melamine-formaldehyde as a flame retarding finishing system for cotton

Charles Q. Yang[*,†], Weidong Wu and Yan Xu

Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, GA 30602, U.S.A.

SUMMARY

In previous research, it was found that melamine-formaldehyde resin can be used as a binder for a hydroxy-functional organophosphorus flame retarding agent (FR) on cotton. The role that trimethylol melamine (TMM) plays in this flame retarding system was studied. When TMM is applied to cotton, it forms crosslinks between cellulose molecules. When TMM is applied to cotton in the presence of FR, it reacts with FR to form a crosslinked polymeric network in addition to reacting with cotton. The formation of the crosslinked network improves the laundering durability of FR and also increases the fabric stiffness. The number of crosslinks among cotton cellulose formed by TMM decreases as the FR concentration in the system is increased. TMM also functions as a nitrogen provider to enhance the flame retarding performance of FR due to phosphorus–nitrogen synergism. Therefore, the amount of TMM used in a FR/TMM formula plays the most critical role in determining the effectiveness of this flame retarding system. The finish bath pH also plays a significant role in influencing the performance of the flame retarding system on cotton. The optimum pH was found to be around 4. Copyright © 2004 John Wiley & Sons, Ltd.
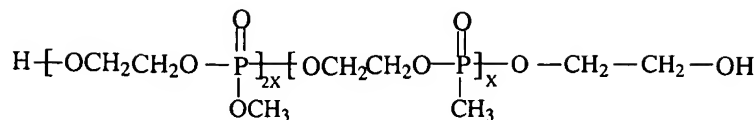
1. INTRODUCTION

Reactive organophosphorus compounds, such as dimethyl(N-hydroxymethyl-carbamoylethyl) phosphonate (DMHP) and its commercial versions with the trade name 'Pyrovatex CP', are among the most commonly used flame retarding finishes for cotton [1–3]. In the presence of an acidic catalyst, the methylol group of DMHP reacts with the hydroxyl group of cotton cellulose to form an acetal linkage, whereas TMM is used in the system to enhance its flame retarding performance by phosphorus–nitrogen synergism [4].

In previous research, a flame retarding system was developed based on a hydroxy-functional organophosphorus oligomer with the commercial name 'Fyroltex HP', shown in Scheme I (CAS Register No. 70715-06-9, abbreviated as FR here), as the flame retarding agent. Since FR does not have a functional group to react with cotton cellulose as does DMHP, it is necessary to use a

---

*Correspondence to: Dr C. Q. Yang, Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, GA 30602, U.S.A.
†E-mail: cyang@fcs.uga.edu

Copyright © 2004 John Wiley & Sons, Ltd.

$$H+OCH_2CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OCH_3}{|}}{P}}\underset{2x}{\}}\{OCH_2CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}\underset{x}{\}}O-CH_2-CH_2-OH$$

Scheme I. Structure of FR.

bonding agent, such as a polycarboxylic acid, dimethyloldihydroxyleneurea (DMDHEU) or TMM, to react with both FR and cotton so that the flame retarding system can become durable to multiple laundering cycles [5–11].

TMM is the reaction product of melamine and formaldehyde in slightly alkaline conditions. In the past, TMM was used as the crosslinking agent for cotton to produce wrinkle-resistant cotton fabrics and also as the crosslinking agent for wood pulp cellulose to improve wet strength retention of paper and paper products [12,13]. TMM is also able to self-condense between methylol and amine groups to form a polymer with methylene bridges [14].

This research studied the role that TMM plays in the FR-based flame retarding system, evaluated the flame retarding performance of cotton fabrics treated with the FR/TMM system, and also determined the optimum finish bath pH for TMM to react with FR and cotton.

2. EXPERIMENTAL

2.1. Materials

Two fabrics were used in this study: (1) a desized, scoured and bleached plain weave 40×40 cotton printcloth weighing $108\,g/m^2$ (Testfabrics Style 400), which was used in most of the experiments; and (2) a 3/1 twill weave 100% cotton fabric ($242\,g/m^2$) dyed with vat dyes (S/5570 C/4551) without softener treatment supplied by Milliken, Blacksburg, South Carolina. FR was a commercial product ('Fyroltex HP') supplied by Akzo Nobel Chemicals, Dobbs Ferry, New York. TMM was a commercial product with the trade name 'Aerotex M-3' supplied by Noveon, Cleveland, Ohio. The catalyst was a NH_4Cl-based commercial product with the trade name 'Catalyst RD' supplied by Eastern Color & Chemical, Greenville, South Carolina.

2.2. Fabric treatment and home laundering procedures

The fabric was first immersed in a finish solution containing TMM or FR/TMM and the catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2.5 min. The amount of catalyst was 2% of TMM by weight. All the concentrations presented here are based on the weight of bath (w/w, %) and the concentrations of FR and TMM presented here are based on 100% solid. The wet pick-up of the plain weave cotton fabric was approximately 105% ± 4%. The wet pick-up of the twill weave fabric was approximately 80% ± 3%. After curing, the treated cotton fabric was subjected to different numbers of home laundering washing/drying (HLWD) cycles with the use of 'AATCC Detergent 1993'. The home laundering procedure was done according to AATCC Test Method 124-1996. The water temperature for laundering was approximately 46°C.

2.3. Fabric performance evaluation

The vertical flammability of the cotton fabric was measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM Standard Method D2863-00. The tensile strength of the fabric was measured according to ASTM Standard Method D5035-95. The conditioned wrinkle recovery angle (WRA) was measured according to AATCC Standard Method 66-1996. The stiffness of the fabric was measured according to ASTM Standard Method D1388-96. The fabric tensile strength, WRA and flexural rigidity were evaluated using the fabric samples after one laundering cycle.

2.4. Determination of phosphorus concentration on the treated cotton fabric

Approximately 2 g of a treated cotton fabric sample taken from four different parts of a specimen were ground in a Wiley mill to a powder to improve sample uniformity. 2 ml of concentrated H_2SO_4 was added to 0.1 g of cotton powder. 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO_3 vapor was produced. The completely digested cotton sample as a clear solution was transferred to a 50 ml volumetric flask, then diluted with distilled/deionized water. The sample thus prepared was analysed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus concentration. This experimental procedure was developed in the laboratory of AKZO Nobel Chemicals.

3. RESULTS AND DISCUSSION

The plain weave cotton fabric was treated with TMM at different concentrations and also with a combination of 30% FR and TMM at different concentrations, then cured at 165°C for 2.5 min. The conditioned WRA of the cotton fabric thus treated was plotted against the TMM concentration (Figure 1). The untreated cotton fabric had a WRA of 205°. The WRA increased to 222° when the fabric was treated with 1% M-F, and it increased further to 280° as the TMM concentration was increased to 10% (Figure 1). The data presented here indicate that TMM functioned as a crosslinking agent for cotton, thus imparting wrinkle resistance to the cotton fabric. The data also show that the amount of the crosslinks increased, as indicated by the increasing fabric WRA in Figure 1, when the concentration of TMM increased.

The percent tensile strength retention in the filling direction of the fabric treated with TMM at different concentrations is shown in Figure 2. The strength retention of the treated fabric decreased from 96% to 71% as the TMM concentration increased from 1% to 10% (Figure 2). In our previous research, it was found that the crosslinking of cotton cellulose molecules reduced the strength of the crosslinked cotton fabric [15,16]. Therefore, the decrease in the fabric tensile strength retention shown in Figure 2 is consistent with the increase in WRA shown in Figure 1, confirming the crosslinking of cotton by TMM.

The WRA and tensile strength retention of the cotton fabric treated with a combination of 30% FR and TMM at different concentration was obviously different from those treated with TMM alone, as shown in Figures 1 and 2, respectively. In the presence of FR, the WRA of the
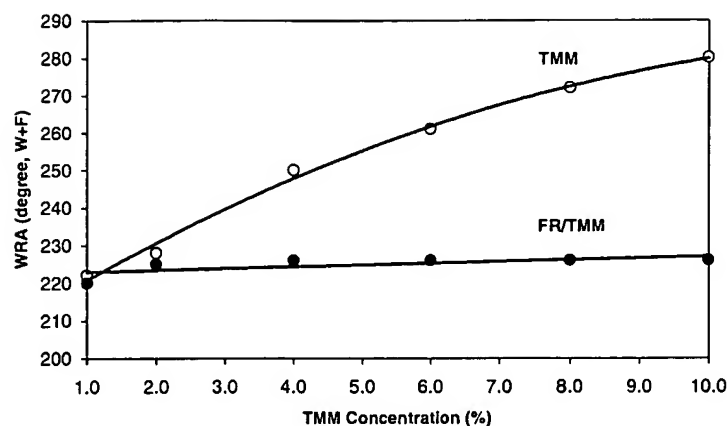
Figure 1. The WRA of the cotton fabric treated with TMM and a combination of 30%
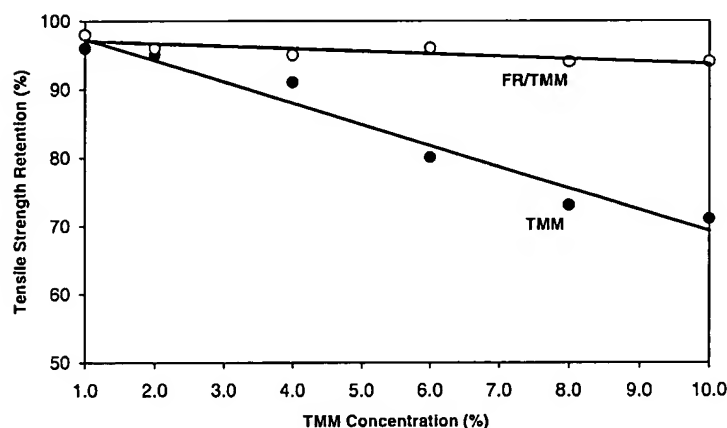FR and TMM, and cured at 165°C for 2.5 min.

Figure 2. The tensile strength retention of the cotton fabric treated with TMM and a combination
of 30% FR and TMM, and cured at 165°C for 2.5 min.

treated fabric remained statistically unchanged at 220°–226° and the tensile strength retention
also remained in the 98%–94% range as the TMM concentration was increased from 1% to
10%. The different performance of the cotton fabric treated with FR/TMM was evidently due
to the reaction between FR and TMM. The hydroxyl groups of FR competed with those of
cotton cellulose to react with the methylol groups of TMM. Consequently, the number of
crosslinks between the cellulose molecules reduced significantly when FR was present on the
fabric. The fact that the WRA and percent strength loss of the fabric treated with FR/TMM
remained at a very low level (approximately 220° and 4%, respectively) and that the WRA and
strength loss of the treated fabric did not have a noteable increase as the TMM concentration
was increased, as shown in Figures 1 and 2, respectively, indicated that the amount of crosslinks
formed on the cotton was small even at high TMM concentrations (6%–10%) when a high
concentration (30%) of FR was present [10].

The cotton fabric was treated with a combination of 30% FR and TMM at different concentrations, cured at 165°C for 2.5 min, and subjected to one and ten laundering cycles. The phosphorus content of the fabric thus treated was plotted against the TMM concentration in Figure 3. The amount of FR bound to the cotton fabric increased as the TMM concentration was increased, as indicated by the increase in the phosphorus concentration on the fabric after laundering (Figure 3). The phosphorus content of the treated fabric increased from 0.62% to 3.30% after one laundering cycle when the TMM concentration was increased from 1% to 10%. Thus, the data presented demonstrate that TMM functions as a binding agent between FR and cotton.

The data presented in Figure 3 also show that the percent retention of FR on the cotton fabric after ten home laundering cycles became higher as the TMM concentration was increased. The fabric treated with 1% TMM had 0.23% phosphorus after ten laundering cycles, which represented a retention of 37% of the phosphorus on the fabric after one laundering cycle. When 6% TMM was used, the phosphorus content on the fabric increased to 2.45% after ten home laundering cycles, which was 93% retention of the phosphorus after one laundering cycle. The percent retention of phosphorus after ten laundering cycles remained unchanged as the TMM concentration was increased further to 10%. Thus, the data in Figure 3 demonstrate that the laundering durability of the FR on the cotton fabric significantly improved as the TMM concentration was increased.

The flexural rigidity of the cotton fabric treated with TMM and that treated with FR/TMM is presented as a function of the TMM concentration in Figure 4. The flexural rigidity of the untreated fabric was 29 mg·cm. When the fabric was treated with TMM, the flexural rigidity increased slightly from 36 to 44 mg·cm as the TMM concentration was increased from 1% to 10% (Figure 4). Melamine reacts with formaldehyde in weakly alkaline aqueous media to form methylol compounds such as TMM. Condensation reactions of TMM take place under neural and acidic conditions to form a polymer, as shown in Scheme II [17]. The data presented in Figure 4 indicate that when TMM was applied to the cotton fabric at increasing concentrations,
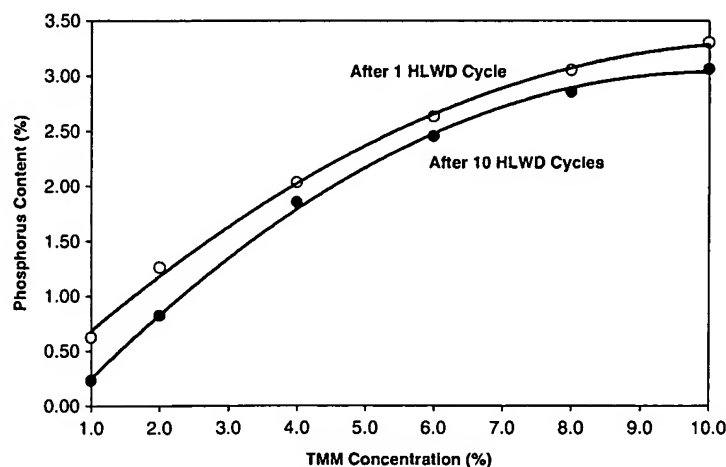

Figure 3. The phosphorus content of the cotton fabric treated with a combination of 30% FR and TMM, and cured at 165°C for 2.5 min.
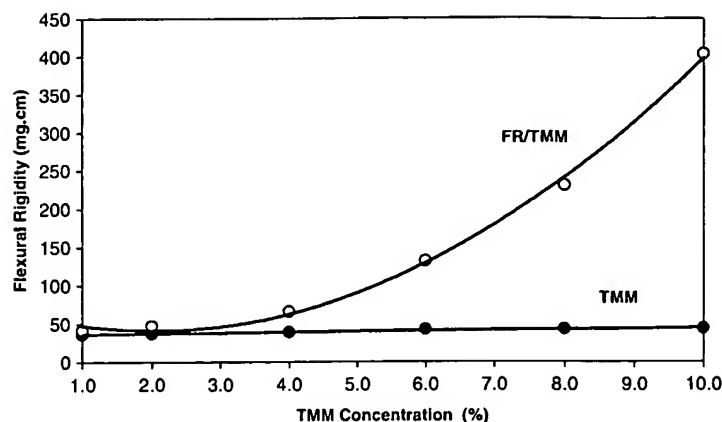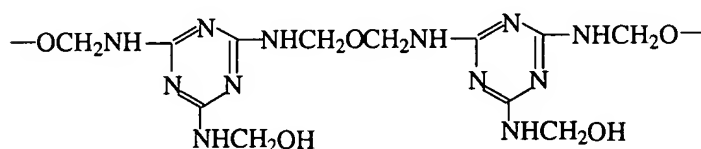
Figure 4. The flexural rigidity of the cotton fabric treated with TMM and a combination
of 30% FR and TMM, and cured at 165°C for 2.5 min.

Scheme II. Self-condensation product of TMM.

the possible self-condensation of TMM did not significantly increase the fabric stiffness. A probable explanation is that the self-condensation product of TMM, if it is formed on the fabric, may have a linear or branched structure instead of a 3-dimensional crosslinked one, thus causing little fabric stiffening effect.

For the fabric treated with a combination of 30% FR and TMM, however, the fabric flexural rigidity had a 10-fold increase from 41 to 403 mg·cm as the TMM concentration was increased from 1% to 10% (Figure 4). The drastically increased stiffness for the fabric as a result of an increase in TMM concentration shown in Figure 4 indicates that TMM (a trifunctional hemiacetal) reacted with the FR (a bifunctional alcohol) to form a crosslinked polymeric network, shown in Scheme 3, as the TMM concentration was increased above 4%. FR became a part of the crosslinked polymeric network, which was bound to cotton through multiple acetal linkages between TMM and cotton. The formation of the crosslinked polymeric network improved the laundering durability of the FR on the fabric. This hypothesis is consistent with the data presented in Figure 3, which shows that the laundering durability of the treated cotton fabric increased as the TMM concentration was increased and it reached the maximum, as the TMM concentration was increased to 6% and higher.

The cotton fabric was treated with a combination of 6% TMM and FR at concentrations ranging from 4% to 42%, and cured at 165°C for 2.5 min. The flexural rigidity of the cotton fabric thus treated is presented as a function of the FR concentration in Figure 5. The flexural rigidity of the fabric treated with 4% FR and 6% TMM (34 mg·cm) was similar to that of the fabric treated with 30% FR without TMM (30 mg·cm). When the concentration of FR increased
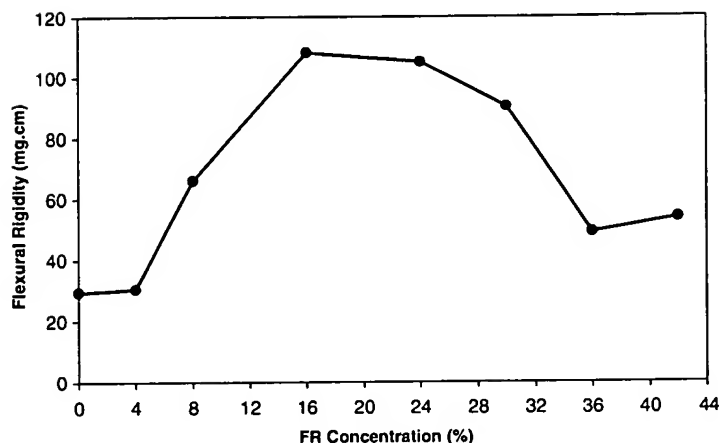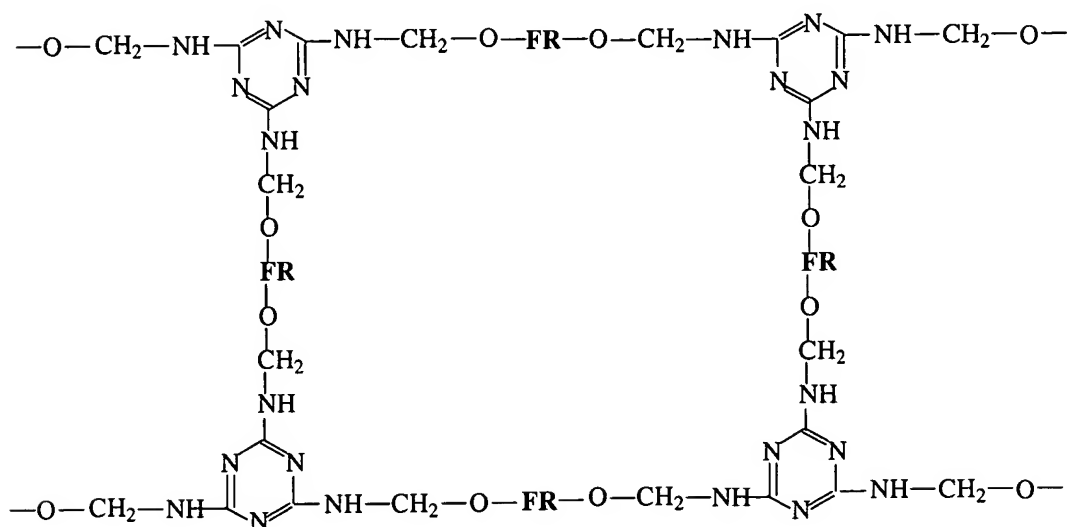
Figure 5. The flexural rigidity of the cotton fabric treated with 6% TMM and FR at different concentrations and cured at 165°C for 2.5 min.

Scheme III. FR/TMM crosslinked polymeric network.

from 4% to 16% and the mole ratio of FR/TMM, assuming $x = 1$ in Scheme I, increased from 0.36 to 1.45 accordingly, the flexural rigidity of the fabric was drastically increased from 34 mg·cm to its maximum at 108 mg·cm (Figure 5). Thus, the data presented in Figure 5 support the hypothesis that the crosslinked polymeric network of FR/TMM, as shown in Scheme III, formed on the cotton fabric within a certain FR/TMM mole ratio range.

When the FR concentration was further increased, the fabric flexural rigidity started to decrease (Figure 5). This is probably because as more FR became available for reaction with TMM, the number of terminal hydroxyl groups of the FR/TMM condensation product

increased, whereas the number of terminal methylol groups of TMM for further reacting with FR to form the crosslinked network decreased. As a result, the formation of the crosslinked network decreased and the fabric flexural rigidity declined accordingly. When the FR concentration was increased to 36%, the fabric flexural rigidity decreased to 49 mg·cm (Figure 5), indicating that the amount of the crosslinked polymeric network formed under such as a condition became insignificant. The data presented in Figure 5 support the hypothesis that FR/TMM formed a crosslinked polymeric network on the fabric discussed above.

The cotton fabric was treated with 30% FR in combination with TMM at different concentrations and cured at 165°C for 2.5 min. The LOI of the fabric thus treated before laundering is presented as a function of the TMM concentration in Figure 6. The LOI (before laundering) increased from 29.8% to 35.5% as the TMM concentration was increased from 1% to 10%, respectively, as shown in Figure 6. All the FR/TMM solutions used to treat the cotton fabric samples contained the same FR concentration (30%) but different TMM concentrations. In our previous research, it was found that the LOI of the cotton fabric treated with 6% TMM was identical to that of the control, thus it was concluded that TMM by itself is not a flame retarding chemical [9]. The increasing LOI of the fabric shown in Figure 6 clearly indicates that the presence of the nonflame-retardant TMM in the system enhanced the flame retarding performance of FR on the treated cotton fabric. The effects of a non-flame retarding additive to enhance the performance of a flame retarding agent fits one of the two definitions for synergism described in the literature [4].

The LOI of the cotton fabric was treated with FR/TMM and subjected to one and ten laundering cycles is also plotted against the TMM concentration in Figure 6. The LOI of the fabric treated with 30% FR and 1% TMM was 29.8%, and it decreased to 21.0% after one laundering cycle (Figure 6). This was because at such a low TMM concentration, most of the FR applied to the cotton fabric was not bound to the fabric and consequently was removed during laundering. When the TMM concentration was increased to 4%, the LOI of the fabric thus treated decreased from 32.5% before washing to 30.2% and 28.3% after one and ten laundering cycles, respectively. When the TMM concentration was further increased to 8%, the fabric's LOI was increased to 33.6% and 32.7% after one and ten laundering cycles, respectively
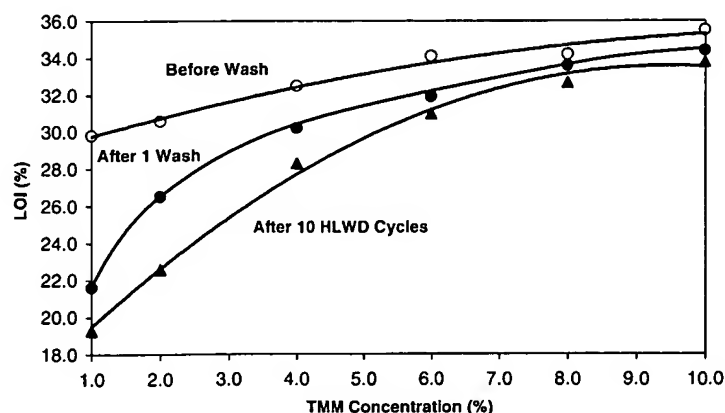

Figure 6. The LOI of the cotton fabric treated with 6% TMM and FR at different concentrations and cured at 165°C for 2.5 min.

(Figure 6). The drastically increased LOI of the treated fabric as a result of higher TMM concentration is attributed to the higher phosphorus retention as shown in Figure 3 and also to the higher enhancement of the flame retarding performance at higher TMM concentration. Because the amount of TMM used in a formula affects both the retention of FR on cotton after multiple laundering cycles and the enhancement of the flame retarding performance of FR by TMM, the TMM concentration is the most critical factor in determining the effectiveness of the FR/TMM flame retarding system.

The effects of the finish bath pH on the reactivity of TMM was studied. The cotton fabric was treated with 30% FR and 8% TMM, and the finish bath pH ranged from 2.0 to 6.0. The percent phosphorus and LOI of the fabric thus treated after one laundering cycle is presented as a function of pH in Figures 7 and 8, respectively. The percent phosphorus on the fabric reached its maximum at pH 4.0 (Figure 7). The effects of the finish bath on LOI show the same trend in
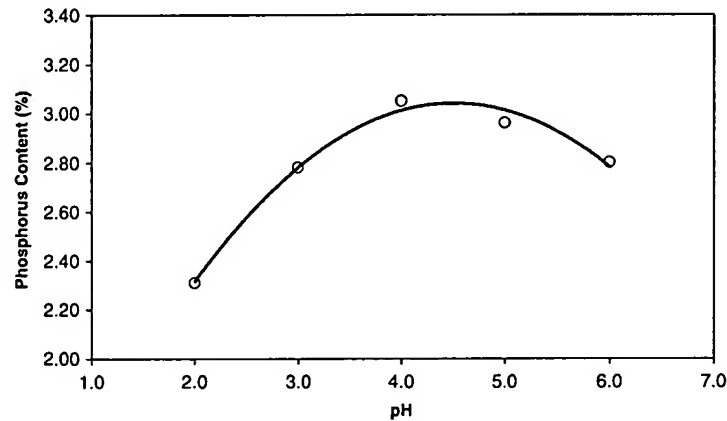

Figure 7. The phosphorus content of the cotton fabric treated with 30% FR and 8% TMM, and cured at 165°C for 2.5 min versus the pH.
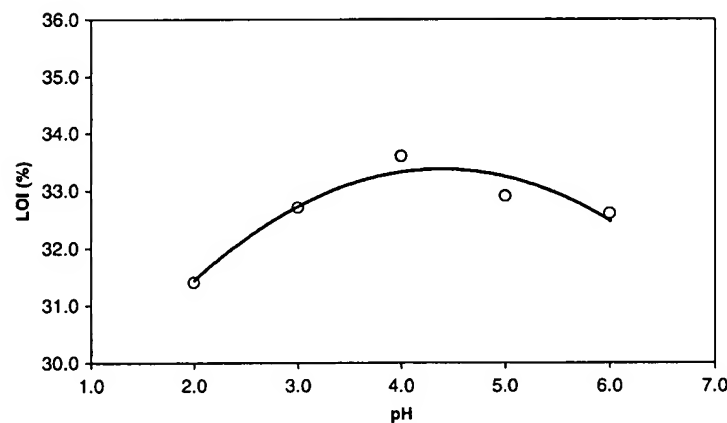

Figure 8. The LOI of the cotton fabric treated with 30% FR and 8%, and cured at 165°C for 2.5 min versus the pH.

Figure 8. Therefore, the finish bath pH plays an important role in the reaction of TMM with FR and cotton. Obviously, the optimum pH for TMM to bond FR to cotton and consequently the optimum pH to achieve the best performance of the FR/TMM flame retarding system is around 4.0.

A twill cotton fabric was used for the evaluation of the performance of the FR/TMM system. The twill fabric was treated with a combination of 30% FR and TMM at concentrations ranging from 1% to 8%, then cured at 165°C for 2.5 min. The LOI and char length of the treated fabric after different numbers of home laundering cycles is shown in Table I. The fabric treated with 30% FR and 2% TMM passed the vertical flammability test after one laundering cycle with a LOI of 26.2%. When the TMM concentration was increased to 4%, the flame retarding performance of the treated fabric increased significantly. The treated fabric had a LOI of 26.8% and passed the vertical flammability test after 40 laundering cycles. When the TMM concentration was increased to 6%, the fabric maintained high flame retarding performance with a LOI of 30.5% and a char length of 89 mm after 40 laundering cycles. The performance of the treated fabric became even higher as the TMM concentration was increased further to 8% (Table I). Thus, the data clearly demonstrate that the FR/TMM system delivers high levels of flame retarding performance and laundering durability when the TMM concentration was 4% or higher (Table I).

The flexural rigidity, tensile strength and WRA of the treated cotton fabric are presented in Table II. When the TMM concentration was 2%, the flexural rigidity of the treated fabric was

Table I. The flammability of the twill cotton fabric treated with 30% FR and TMM at different concentrations, and cured at 165°C for 2.5 min.

TMM concentration (%)	LOI (%)						Char length (mm)				
	Before wash	1 HLWD	5 HLWD	10 HLWD	20 HLWD	40 HLWD	1 HLWD	5 HLWD	10 HLWD	20 HLWD	40 HLWD
1	30.0	22.8	—	—	—	—	>300	—	—	—	—
2	31.1	26.2	—	—	—	—	117	—	—	—	—
4	32.6	30.4	30.1	29.8	28.1	26.8	62	64	72	76	125
6	34.5	33.0	32.9	32.5	31.2	30.5	54	58	72	74	89
8	36.1	35.0	34.5	34.2	33.8	33.0	49	58	74	63	71

Table II. The flexural rigidity, tensile strength and WRA of the twill cotton fabric treated with 30% FR and TMM with different concentrations, and cured at 165°C for 2.5 min.

TMM concentration (%)	Flexural rigidity (mg·cm)	Tensile strength (filling, kgf)	Tensile strength retention (filling, %)	WRA (degree, w + f)
Control	438	43.9	—	166
1	568	42.3	96	181
2	597	40.3	92	210
4	895	37.5	85	210
6	1720	37.4	85	211
8	3908	36.6	83	212

Table III. The phosphorus retention of the twill cotton fabric treated with 30% FR and TMM at different concentrations, and cured at 165°C for 2.5 min.

TMM concentration (%)	Phosphorus content (%)				Phosphorus retention (%)		
	Before wash	1 HLWD	5 HLWD	10 HLWD	1 HLWD	5 HLWD	10 HLWD
1	3.36	0.66	—	—	20	—	—
2	3.45	1.18	—	—	34	—	—
4	3.43	1.68	1.55	1.42	49	45	41
6	3.42	2.26	2.10	1.90	66	61	55
8	3.42	2.32	2.38	1.97	68	69	58

597 mg·cm, which is only slightly higher than that of the control sample (438 mg·cm) (Table II). When the TMM concentration was increased to 6%, the flexural rigidity was increased to 1720 mg·cm due to the formation of crosslinked polymeric network of FR/TMM on the fabric as discussed previously.

Table III shows the phosphorus content and percent phosphorus retention of the fabric treated with FR/TMM. When the TMM concentration was 6%, 66% of FR was bound to cotton after one laundering cycle, and 55% of FR was still retained on the fabric after ten laundering cycles (Table III). The data presented here clearly indicate that the FR/TMM system has high levels of laundering durability at higher TMM concentrations, which is consistent with the fabric stiffness data presented in Table II. When the TMM concentration was 4%, the fabric stiffness was acceptable (Table II), whereas it maintained flame retarding performance after 40 laundering cycles (Table I).

The twill cotton fabric treated with FR/TMM also demonstrates high fabric strength retention. When the TMM concentration was in the range 4%–6%, the treated fabric retained 85% strength retention (Table II). When the TMM concentration was increased from 2% to 8%, the fabric WRA remained statistically unchanged. Thus, the data suggest that the additional amount of TMM applied to the fabric reacted with FR to form more crosslinked networks instead of reacting with cotton cellulose to form more crosslinking between cellulose molecules.

4. CONCLUSIONS

When TMM is applied to cotton, it forms crosslinks between cellulose molecules, thus increasing fabric wrinkle resistance. When TMM is applied to cotton in the presence of FR, it reacts with both cotton and FR, thus bonding FR to cotton. As the TMM concentration increases, it reacts with FR to form a crosslinked polymeric network, thus improving the laundering durability of FR. The formation of the crosslinked polymeric network also increases the stiffness of the treated fabric. TMM also functions as a nitrogen provider, thus enhancing the flame retarding performance of FR. Therefore, the TMM concentration in a FR/TMM formula plays the most critical role in determining the effectiveness of the FR/TMM system as a flame retarding finish system because it affects both the amount of the FR bound to cotton and also the magnitude of the enhancement of FR's flame retarding performance due to phosphorus–nitrogen synergism. The FR/TMM system shows an optimum performance at

pH 4. The cotton fabric treated with the FR/TMM system demonstrates excellent flame retarding performance, high laundering durability and low tensile strength loss. The fabric stiffness significantly increases when a high TMM concentration is used. Therefore, the desire for high flame retarding performance must be balanced with that of limiting the fabric stiffness when choosing a FR/TMM formula.

ACKNOWLEDGEMENT

REFERENCES

1. Weil ED. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn, Grayson M (ed.). Wiley: New York, 1991; 10:976–1022.
2. Weil ED. In *Handbook of Organophosphorus Chemistry*, Chapter 14, Engel R (ed.). Marcel Dekker: New York, 1992; 683–738.
3. Horrocks AR. Flame-retardant finishing of textiles. *Reviews in Progress Coloration* 1986; 16:62–101.
4. Lewin M. In *Handbook of Fiber Science and Technology*: Vol. II *Chemical Processing of Fibers and Fabrics, Functional Finishes*, Part B, Lewin M, Sello SB (eds). Marcel Decker: New York, 1984; 60–62.
5. Stowell JK, Weil ED, Coble WL, Yang CQ. Formaldehyde-free flame retardant treatment for cellulose-containing materials. *US Patent 6,365,070 B1*, 2002.
6. Yang CQ, Wu W. Combination of a hydroxy-functional organophosphorus oligomer and a multifunctional carboxylic acid as a flame retardant finishing system for cotton: Part I. The chemical reactions. *Fire and Materials* 2003; 27:223–237.
7. Yang CQ, Wu W. Combination of a hydroxy-functional organophosphorus oligomer and a multifunctional carboxylic acid as a flame retardant finishing system for cotton: Part II. Formation of calcium salt during laundering. *Fire and Materials* 2003; 27:239–281.
8. Wu W, Yang CQ. Correlation between limiting oxygen index and phosphorus/nitrogen content of the cotton fabric treated with a hydroxy-functional orgonophosphorus flame retardant agent and DMDHEU. *Journal of Applied Polymer Science* 2003; 90:1885–1890.
9. Wu W, Yang CQ. Correlation between limiting oxygen index and phosphorus content of the cotton fabric treated with a hydroxy-functional organophosphorus flame retardant agent and melamine-formaldehyde resin. *Journal of Fire Sciences* 2004; 22:11–23.
10. Wu W, Yang CQ. Comparison of DMDHEU and melamine-formaldehyde as the binding system for a hydroxy-functional organophosphorus flame retarding agent on cotton. *Journal of Fire Sciences* 2004; 22:125–142.
11. Stowell JK, Yang CQ. A durable low-formaldehyde flame retardant finish for cotton fabrics. *AATCC Review* 2003; 3:17–20.
12. Heywood DW. In *Chemistry of the Textile Industry*, Carr CM (ed.). Blackie Academic & Professional: London, 1995; 173–175.
13. Chan LL, Lau PWK. In *Wet-Strength Resins and Their Application*. TAPPI Press: Atlanta, Georgia, 1994; 1–14.
14. Stevens MP. In *Polymer Chemistry*, 2nd edn. Oxford University Press: New York, 1990; 483–485.
15. Kang I, Yang CQ, Wei W, Lickfield GC. The mechanical strength of the cotton fabrics crosslinked by polycarboxylic acids: Part I. Acid degradation and crosslinking of cellulose. *Textile Research Journal* 1998; 68: 865–870.
16. Yang CQ, Wei W, Lickfield GC. Mechanical strength of durable press finished cotton fabric: Part III. Change in cellulose molecular weight. *Textile Research Journal* 2000; 70:910–915.
17. Higuchi M. In *Concise Polymeric Materials Encyclopedia*, Salamone JC (ed.). CRC Press: Boca Raton, 1999; 837–838.

Exhibit B

Comparison of DMDHEU and Melamine-formaldehyde as the Binding Agents for a Hydroxy-functional Organophosphorus Flame Retarding Agent on Cotton

WEIDONG WU AND CHARLES Q. YANG*

Department of Textiles, Merchandising and Interiors
The University of Georgia
Athens, GA 30602

(Received June 27, 2003)

ABSTRACT: It is necessary to use a crosslinking agent to bond a flame-retarding hydroxy-functional organophosphorus oligomer (FR) to cotton so that the flame resistance of the treated cotton fabric can be durable to multiple home-laundering. Both dimethyloldihydroxyethyleneurea (DMDHEU) and melamine-formaldehyde (M-F) have been used as the binding agents between FR and cotton. The vertical flammability, limiting oxygen index (LOI) and phosphorus content after different numbers of laundering cycles as well as the wrinkle resistance and tensile strength of the cotton fabric treated with FR/DMDHEU and FR/M-F was investigated and compared in this research. We found that DMDHEU is more effective for crosslinking cotton cellulose and for crosslinking between FR and cotton than M-F. We also found that the bonding formed by DMDHEU between cotton and FR is more durable to multiple laundering cycles than that formed by M-F. M-F is a more effective nitrogen provider than DMDHEU to enhance the flame retarding performance of the treated cotton fabric through phosphorus–nitrogen synergism, therefore the presence of M-F in the flame retardant finishing system significantly increases the flame resistance

*Author to whom correspondence should be addressed.

of the treated fabric. DMDHEU, as an effective crosslinking agent for cotton, causes more fabric strength loss than M-F.
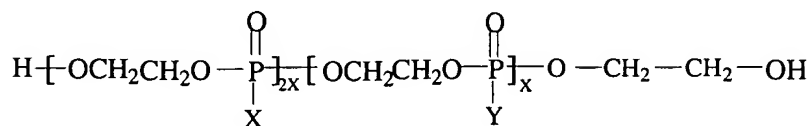
KEY WORDS: cotton, crosslinking, DMDHEU, durable flame retardant finishes, melamine-formaldehyde, organophosphorus chemicals.

INTRODUCTION

REDUCING THE FLAMMABILITY of fibrous materials, such as textile fibers and fabrics, has been one of the major challenges facing the scientific and industrial communities. Flame resistance is a desirable property that can be imparted to cotton fabrics by means of chemical finishing. Currently, the commercially available durable flame retardants for cellulosic fibers include the precondensate/ammonia process (known as "Proban") and reactive organophosphorus flame retardant compounds, such as dimethyl(N-hydroxymethyl-carbamoylethyl) phosphonate and its commercial versions with the trade name of "Pyrovatex CP" [1,2]. To achieve durable flame retarding performance, those reagents were designed to react with cellulosic substrate or to self-condense under conventional finishing conditions. However, the reactive organophosphorus flame retarding system contains significant levels of formaldehyde, a known carcinogen. The "Proban" technology requires the use of an ammoniation chamber, which is not compatible with most of the finishing operations in the industry. Those finishing treatments may also cause excessive fabric strength loss and adverse effects on fabric handle properties [3].

In our previous research, we developed a nonformaldehyde flame retarding system for cotton based on a hydroxy-functional organophosphorus oligomer (FR), such as the one shown in Scheme 1 where X and Y are alkoxy and alkyl groups, as the flame retarding agent and a polycarboxylic acid as the bonding agent [4]. We also studied the chemical reactions on the cotton fabric treated with FR and 1,2,3,4-butanetetracarboxylic acid (BTCA) [5,6].

N-methylol reagents, such as DMDHEU, have long been used in the textile industry as the crosslinking agents for cotton to produce wrinkle-

$$H\text{---}[OCH_2CH_2O\text{---}\overset{\overset{O}{\parallel}}{\underset{X}{P}}]_{2x}[OCH_2CH_2O\text{---}\overset{\overset{O}{\parallel}}{\underset{Y}{P}}]_x O\text{---}CH_2\text{---}CH_2\text{---}OH$$

Scheme 1.

resistant cotton fabrics and garments [7]. M-F resins are used as crosslinking agents for wood pulp cellulose to impart high wet strength retention to paper [8]. M-F is also used as a nitrogen-provider for dimethyl(*N*-hydroxymethyl-carbamoylethyl) phosphonate [9].

In our previous research, we investigated the correlation between LOI and the phosphorus content of the cotton treated with the FR/DMDHEU and FR/M-F systems [10,11]. In this research, we studied and compared the reactivity of DMDHEU and M-F in the flame retarding systems based on FR, examined the phosphorus–nitrogen synergism, and evaluated the flame retarding performance as well as strength retention of the cotton fabric treated with two different flame retarding systems.

EXPERIMENTAL

Materials

The fabric used was a desized, scoured, and bleached 40 × 40 cotton printcloth weighing 108 g/m^2 (Testfabrics Style 400). The hydroxy-functional organophosphorus oligomer with the commercial name of "Fyroltex HP" (shown in Scheme 1) was supplied by Akzo Nobel Chemical Inc., Dobbs Ferry, New York. DMDHEU with the commercial name of "Freerez 900" was supplied by Noveon, Cleveland, Ohio. The trimethylolated M-F resin with the trade name of "ECCO REZ M-300" was supplied by Eastern Color & Chemical Company, Greenville, South Carolina. The catalysts (NH$_4$Cl and H$_3$PO$_3$) were reagent-grade chemicals supplied by J. T. Baker, New Jersey, and Aldrich, Wisconsin, respectively.

Fabric Treatment and Home Laundering Procedures

The fabric was first immersed in a finish solution containing FR, DMDHEU (or M-F) and a catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2.5 min. NH$_4$Cl and H$_3$PO$_3$ were used as the catalysts for DMDHEU and M-F, respectively. The weight ratios of NH$_4$Cl/DMDHEU and H$_3$PO$_3$/M-F were 0.04 and 0.03 in all the formulas, respectively. All the concentrations presented here are based on weight of bath (w/w, %). Both the concentrations (w/w) of DMDHEU and M-F are based on 100% solid. The wet pick-up of the cotton fabric was approximately 105 ± 3%. After curing, the treated

cotton fabric was subjected to a different number of home laundering washing/drying (HLWD) cycles with the use of "AATCC Standard Detergent 1993". The home laundering procedure was done according to *AATCC Test Method* 124-1996 ("Appearance of Fabrics After Repeated Home Laundering"). The water temperature for laundering was approximately 46°C.

Fabric Performance Evaluation

The vertical flammability of the cotton fabric was measured according to *ASTM Standard Method D6413-99*. The limiting oxygen index (LOI) of the cotton fabric was measured according to *ASTM Standard Method D2863-97*. The tensile strength of the fabric was measured according to *ASTM Standard Method D5035-95*. The conditioned wrinkle recovery angle (WRA) was measured according to *AATCC Standard Method 66-1996*. The fabric tensile strength and WRA were evaluated after one laundering cycle.

Determination of Phosphorus Concentration on the Treated Cotton Fabric

Approximately 2 g of treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Two milliliters of concentrated H_2SO_4 were added to 0.1 g of cotton powder. Ten milliliters of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-mL volumetric flask, then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus concentration.

RESULTS AND DISCUSSION

The cotton fabric was treated with DMDHEU/NH_4Cl and M-F/H_3PO_3 at different concentration levels individually, and then cured at 165°C for 2.5 min. The conditioned WRA of the cotton fabric treated with DMDHEU and that treated with M-F is plotted against the concentra-

tion of the crosslinker in Figure 1. For both the fabric treated with DMDHEU and that treated with M-F, the WRA increased as the concentration of crosslinkers was increased (Figure 1). The WRA of the cotton fabric treated with DMDHEU is evidently much higher than that treated with M-F, and the difference in WRA between the two crosslinkers increased as their concentration was increased (Figure 1). The WRA of the fabric treated with 5% DMDHEU is 33° higher than that treated with 5% M-F. The significantly higher WRA for the fabric treated with DMDHEU demonstrates that DMDHEU is more reactive for crosslinking cotton than M-F.

DMDHEU (Scheme 2) has four hemi-acetal groups to react with the hydroxyl groups of cellulose to form crosslinking among cellulose molecules. The two groups derived from formaldehyde in a DMDHEU molecule are significantly more reactive than those derived from glyoxal.

Methylolated melamine, a class of formaldehyde-based melamine resin (M-F), is the reaction product of melamine and formaldehyde at
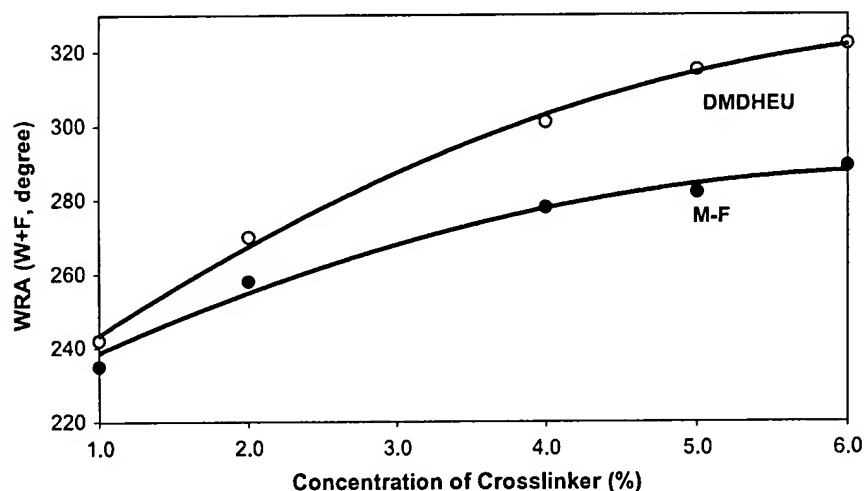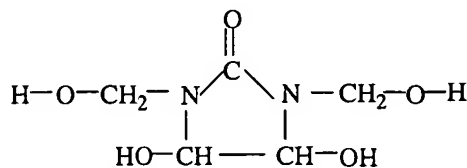

Figure 1. The WRA of cotton fabric treated with DMDHEU or M-F at different concentrations and cured at 165°C for 2.5 min.
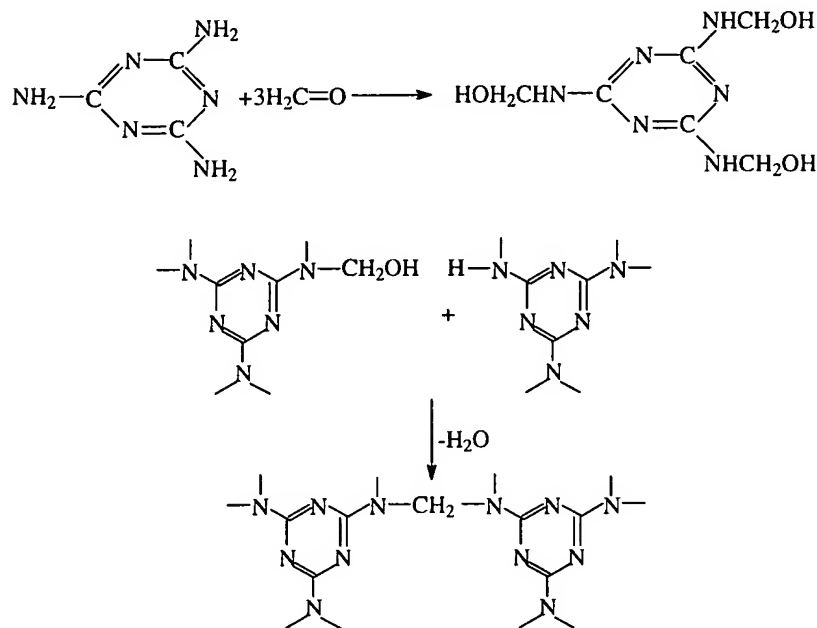

Scheme 2.

slightly alkaline conditions (Scheme 3). It is able to self-condense between methylol and amine groups to form a polymer with methylene bridges [12], shown in Scheme 3, in addition to forming crosslinkages between cellulosic hydroxyl groups on cotton. Consequently, M-F is a less-efficient crosslinking agent for cotton than DMDHEU as indicated by the lower WRA of the treated cotton fabric shown in Figure 1.

The cotton fabric was also treated with 32% FR in combination with DMDHEU or M-F at different concentration levels, then cured at 165°C for 2.5 min. The conditioned WRA of the fabric thus treated is shown as a function of the concentration of the crosslinker in Figure 2. For both DMDHEU and M-F, the WRA of the treated fabric significantly decreased as the FR was present in the treatment solutions. The WRA of the fabric treated with 5% DMDHEU was 315°, and it decreased to 295° when the fabric was treated with 5% DMDHEU and 32% FR (Figure 2). This was an indication that the hydroxyl of the FR competed with cellulosic hydroxyl to react with DMDHEU, thus reducing the amount of crosslinkages among cellulose molecules.

The WRA of the cotton fabric treated with M-F increased from 231 to 289° as the M-F concentration increased from 1.0 to 6.0% (Figure 1). The WRA of the cotton fabric treated with FR/M-F was drastically
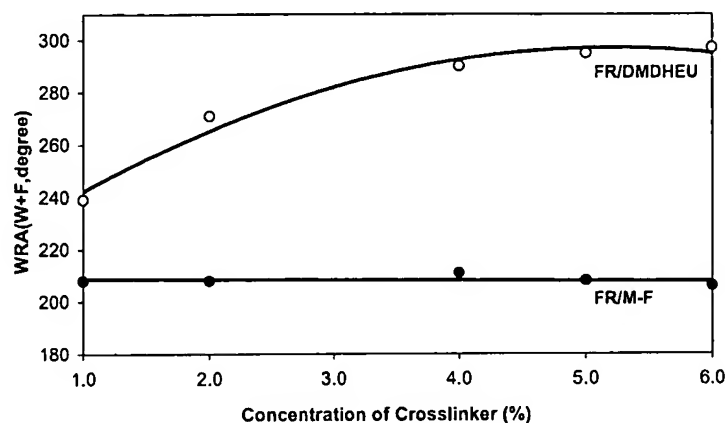

Scheme 3.

Figure 2. The WRA of cotton fabric treated with 32% FR and a crosslinker at different concentrations and cured at 165°C for 2.5 min.

reduced when 32% FR was present together with M-F. Figure 2 shows that the WRA of the fabric treated with FR/M-F remained practically unchanged as the concentration of M-F was increased from 1.0 to 6.0% (Figure 2). The WRA of the fabric treated with FR/M-F in the 206–211° range is very close to that of the control fabric (around 200°), thus indicating that in the presence of 32% FR, the overwhelming majority of M-F reacted with FR, self-condensed or singly bound to cellulose, and the amount of M-F crosslinking cotton was insignificant.

The tensile strength in the filling direction of the cotton fabric treated with M-F at different concentrations and that treated with 32% FR and M-F at different concentration levels, and cured at 165° for 2.5 min is shown in Figure 3. As the concentrations of M-F increased from 1.0 to 6.0%, the fabric strength decreased from 16.2 to 13.5 kg while the tensile strength of the control sample was 16.8 kg (Figure 3). The reduction of the fabric tensile is a result of crosslinking of cellulose molecules by M-F, since crosslinking cellulose reduced the tensile strength of cotton fabrics [13]. When 32% FR was present in combination with M-F, the tensile strength of cotton fabric thus treated remained unchanged in the same M-F concentration range (1.0–6.0%) (Figure 3). The nearly 100% fabric strength retention confirms that in the presence of 32% FR, the amount of M-F crosslinking on the cotton was insignificant.

Presented in Figure 4 is the tensile strength in the filling direction of cotton fabric treated with DMDHEU and that treated with 32% FR and DMDHEU at different concentrations and cured at 165° for 2.5 min. The data show that the presence of FR together with DMDHEU significantly reduced the fabric strength loss due to the reaction between DMDHEU
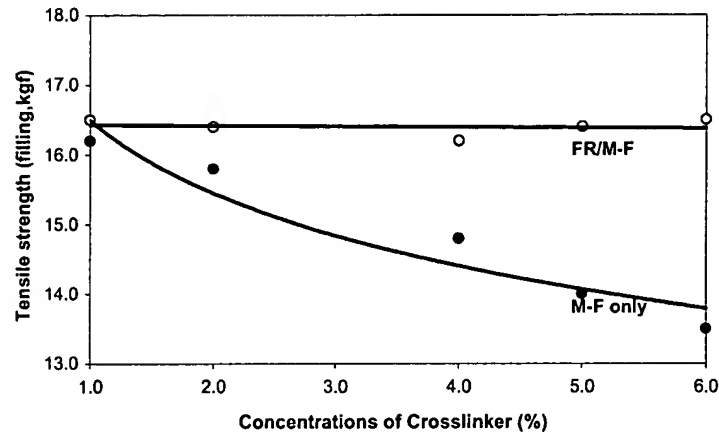
Figure 3. The tensile strength in the filling direction of the cotton fabric treated with 32% FR in combination with M-F of different concentrations, and that treated with M-F of different concentrations, and cured at 165°C for 2.5 min.
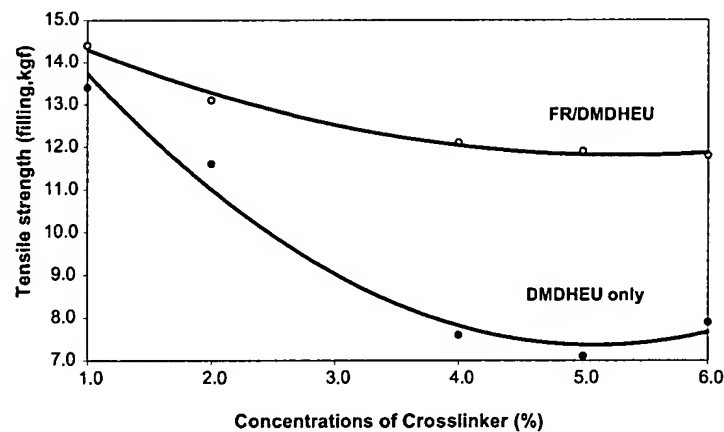

Figure 4. The tensile strength in the filling direction of the cotton fabric treated with 32% FR in combination with DMDHEU of different concentrations, and that treated with DMDHEU of different concentrations, and cured at 165°C for 2.5 min.

and FR, which reduces the amount of crosslinking of cellulose formed by DMDHEU.

The percent phosphorus content of the cotton fabric treated with 32% FR in combination with DMDHEU or M-F at different concentration levels, cured at 165°C for 2.5 min, and subjected to 1 and 12 home laundering cycles is presented in Figures 5 and 6, respectively. The cotton fabric treated with 32% FR contained 5.26% phosphorus before laundering. The cotton fabric treated with 32% FR and 1.0%

DMEHEU had 1.64% phosphorus (31% retention) after one laundering cycle, and the phosphorus content increased to 4.38% (83% retention) when the DMDHEU concentration increased to 10% (Figure 5). For the cotton fabric treated with FR/M-F, its phosphorus concentration increased from 1.10% (21% retention) to 2.80% (53% retention) when
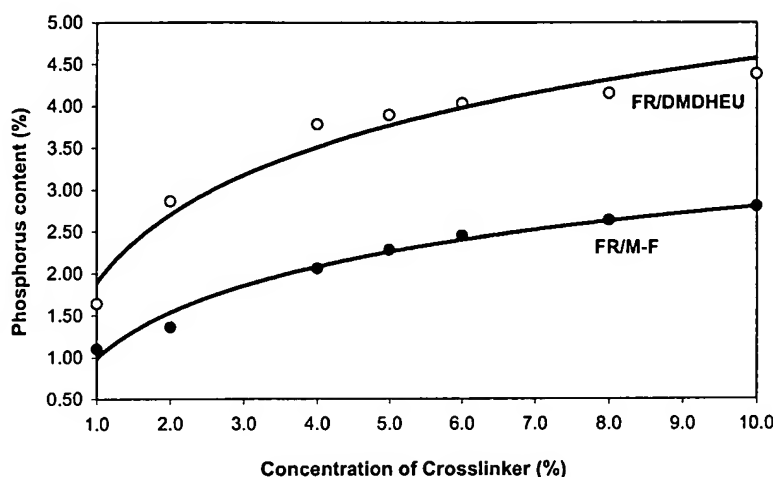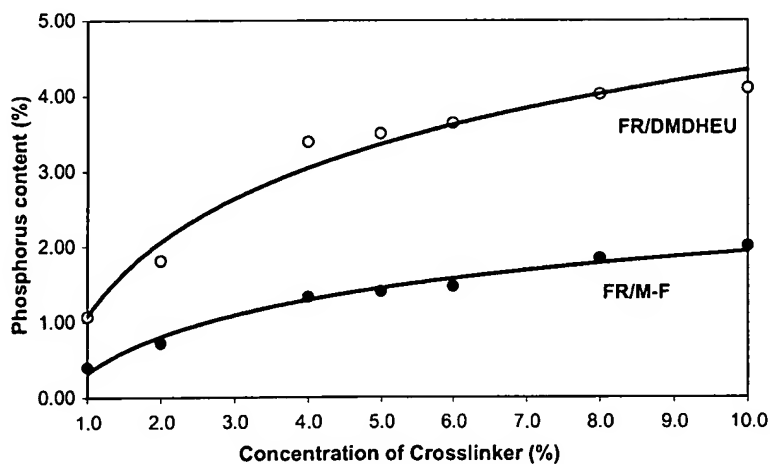
Figure 5. The phosphorus content of the cotton fabric treated with 32% FR in combination with a crosslinker (DMDHEU or M-F) at different concentrations, cured at 165°C for 2.5min and subjected to 1home laundering cycle.

Figure 6. The phosphorus content of the cotton fabric treated with 32% FR in combination with a crosslinker (DMDHEU or M-F) at different concentrations, cured at 165°C for 2.5min and subjected to 12home laundering cycle.

the M-F concentration was raised from 1.0 to 10% (Figure 5). The amount of FR bound to the cotton fabric by DMDHEU is notably higher than that bound by M-F. Thus, the data clearly indicate that DMDHEU is more efficient for binding FR to cotton.

After the treated cotton fabric was subjected to 12 home laundering cycles, the phosphorus content on the fabric treated with FR/DMDHEU ranged from 1.07 to 4.10% on the fabric, representing 20–78% retention, when the DMDHEU concentration increased from 1.0 to 10.0%, respectively (Figure 6). When M-F was used as the crosslinker, the phosphorus content increased from 0.40 to 1.84%, representing 8–35% retention, in the same crosslinker concentration range. The data show that the difference in phosphorus content between the cotton fabric treated with FR/DMDHEU and that treated with FR/M-F became more pronounced as the number of home laundering cycles was increased to 12. Thus, the data clearly demonstrate that the bonding between FR and cotton formed by DMDHEU is more durable to home multiple laundering than that formed by M-F.

The LOI of the cotton fabric treated with 32% FR in combination with a crosslinker (DMDHEU or M-F) at different concentrations and cured at 165°C for 2.5 min before laundering is plotted against the concentration of the crosslinker in Figure 7. All the flame-retarding finish solutions used to treat the cotton fabric contained the same concentration (32%) of FR, and the phosphorus of the treated cotton fabric was around 5.3% before laundering. The LOI of the fabric treated with FR/
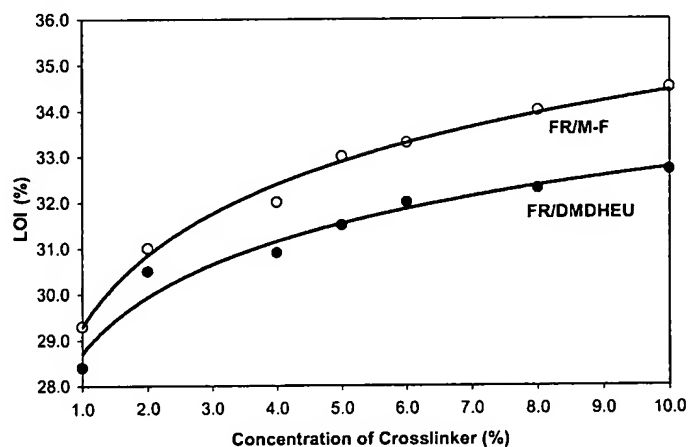

Figure 7. The LOI of the cotton fabric treated with 32% FR and a crosslinker (DMDHEU or M-F) at different concentrations and cured at 165°C for 2.5 min (before wash).

DMDHEU and that treated with FR/M-F increased as the concentration of the crosslinkers increased, thus indicating that both crosslinkers, i.e., DMDHEU and M-F, enhance the flame-retarding performance of the treated cotton fabric. The enhancing effects of a nonflame retarding additive to a flame retarding agent is one of the two definitions for synergism [9]. In our previous research, we found that the cotton fabric treated with 6% M-F has LOI of 17.8, identical to that of untreated fabric [10]. M-F and DMDHEU by themselves are not flame retarding agents. However, they provide phosphorus–nitrogen synergism and enhance the flame retarding performance of FR. The data show that M-F is a more efficient nitrogen provider, because the cotton fabric treated with FR/M-F has significantly higher LOI than that treated with FR/DMDHEU at the same FR and crosslinker concentrations (Figure 7).

The LOI of the treated cotton fabric subjected to one and 12 home laundering cycles is presented as a function of the concentration of the crosslinker in Figures 8 and 9, respectively. One observes that the LOI of the fabric treated with FR/M-F was lower than that treated with FR/DMDHEU when the crosslinker concentration was below 4.0% (Figure 8). The relatively lower LOI for the fabric treated with FR/M-F is due to the relatively lower phosphorus content of the fabric as shown in Figures 5. When the M-F concentration increased to 6.0% and beyond, the LOI of the treated fabric was higher than that treated with FR/DMDHEU (Figure 8). The enhancement in flame retarding performance provided by M-F due to phosphorus–nitrogen synergism
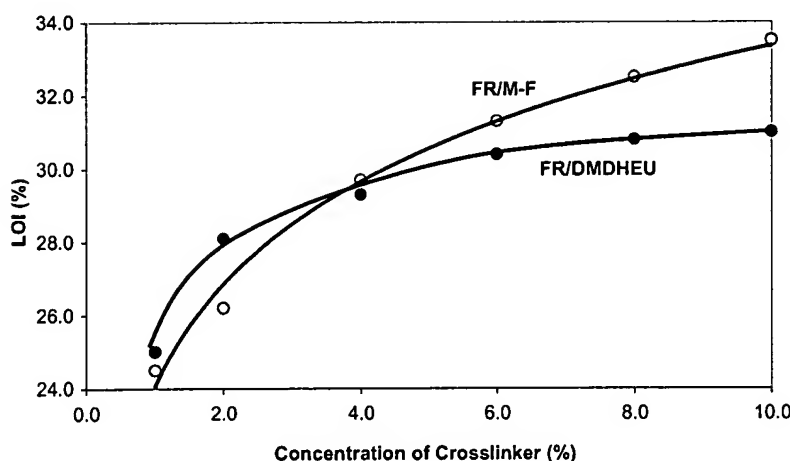
Figure 8. The LOI of the cotton fabric treated with 32% FR and a crosslinker (DMDHEU or M-F) at different concentrations and cured at 165°C for 2.5 min (after one laundering cycle).
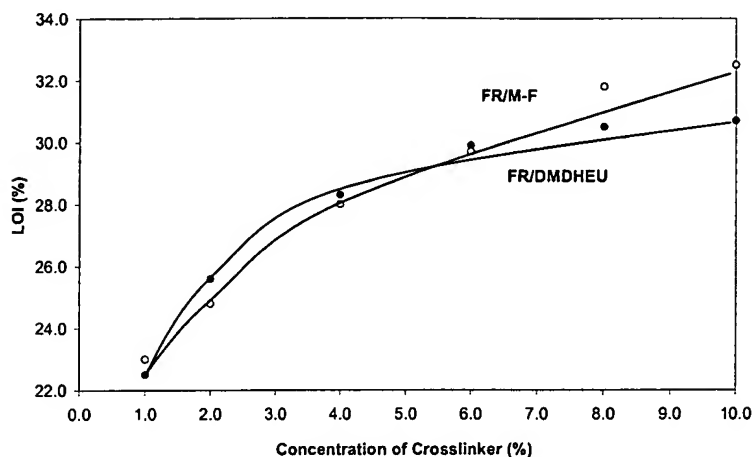
Figure 9. The LOI of the cotton fabric treated with 32% FR and a crosslinker (DMDHEU or M-F) at different concentrations and cured at 165°C for 2.5 min (after 12 laundering cycles).

became more significant at higher M-F concentrations since M-F is a more efficient nitrogen provider. The fact that the difference between the fabric treated with FR/DMDHEU and that treated with FR/M-F became smaller after 12 washes, as shown in Figure 9, is evidently due to the low durability of the FR/M-F system. The vertical flammability of the treated cotton fabric presented in Table 1 is consistent with LOI data shown in Figures 8 and 9.

The cotton fabric was treated FR at different concentrations and 6% crosslinker, and cured at 165°C for 2.5 min. The LOI of the fabric thus treated before laundering is plotted against the FR concentration in Figure 10. The LOI of the cotton fabric treated with FR/M-F increased from 32.8 to 34.1 as the FR concentration increased from 25 to 45%, whereas it increased from 29.7 to 31.9 for the fabric treated with FR/ DMDHEU at the same concentration range (Figure 10). Thus, the data presented in Figure 10 provides additional evidence that M-F is a more effective nitrogen provider for the FR-based flame retarding system.

The phosphorus content of the cotton fabric treated with 6% DMDHEU and FR at the concentration range 25–45% after one home laundering ranged from 3.12 to 4.53%, whereas it was 2.43–3.02% for the fabric treated with FR/M-F at the same concentration (Figure 11). After 12 home laundering cycles, the phosphorus content of the cotton fabric treated with FR/DMDHEU ranged 2.59–3.69%, which is significantly higher than that treated with FR/M-F (1.93–2.31) (Figure 12). The difference in phosphorus content between the fabric treated with

Table 1. The vertical flammability of the cotton fabric treated with 32% FR, in combination with DMDHEU and M-F of different concentrations, and cured at 165°C for 2.5 min.

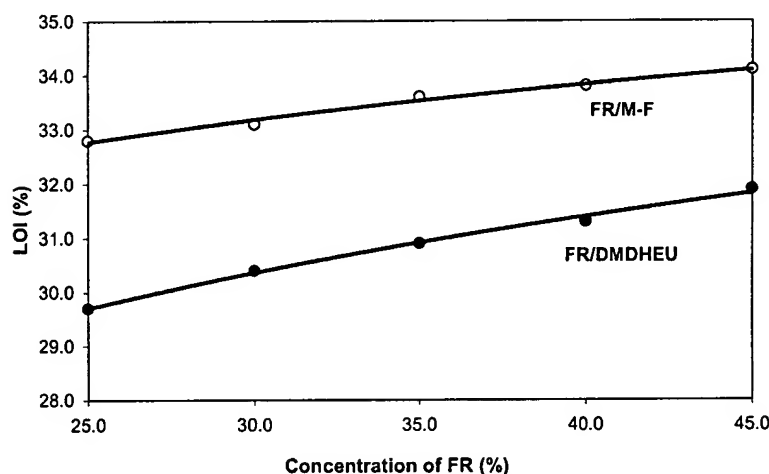|	Char length (mm)	
Crosslinker (%)	After 1 HLTD	After 12 HLTD
DMDHEU 1	128	>300
DMDHEU 2	106	127
DMDHEU 4	98	111
DMDHEU 5	100	105
DMDHEU 6	99	127
DMDHEU 8	94	110
DMDHEU 10	83	93
M-F 1	>300	>300
M-F 2	>300	>300
M-F 4	124	255
M-F 5	130	150
M-F 6	139	114
M-F 8	53	106
M-F 10	77	86

Figure 10. The LOI of the cotton fabric treated with 6% crosslinker in combination with FR at different concentrations (before wash).

FR/DMDHEU and that treated with FR/M-F increased as the number of laundering cycle increased as shown in Figures 11 and 12. The cotton fabric treated with 35% FR and 6.0% DMDHEU retained 3.77% phosphorus after one laundering cycle, which was 36% higher than that
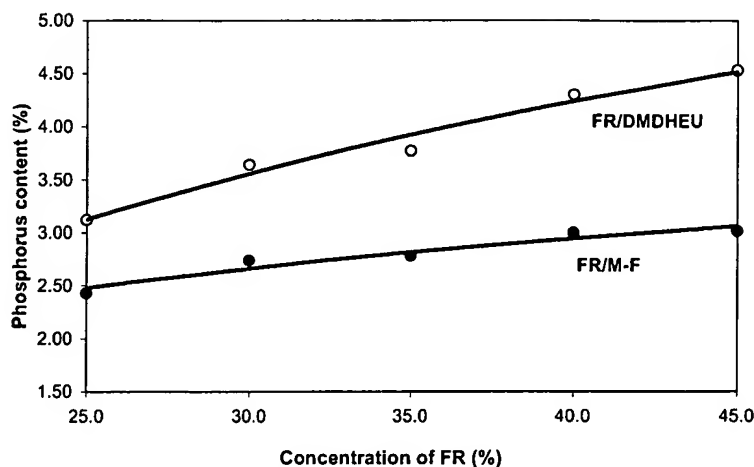
Figure 11. The phosphorus content of the cotton fabric treated with 6% crosslinker in combination with FR at different concentrations (after 1 home laundering cycle).
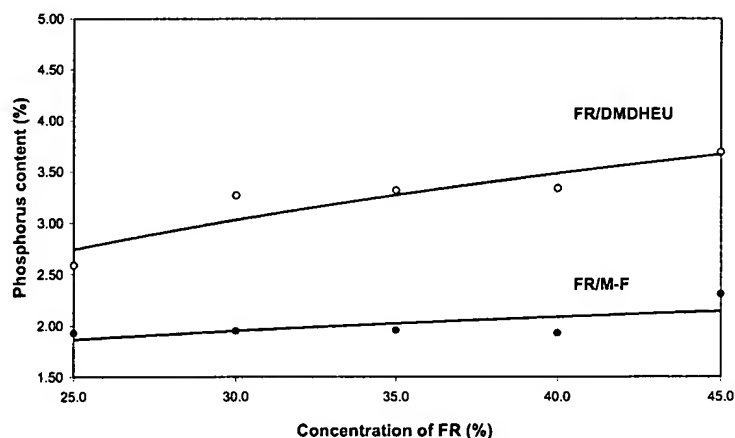

Figure 12. The phosphorus content of the cotton fabric treated with 6% crosslinker in combination with FR at different concentrations (after 12 home laundering cycles).

treated with FR and M-F at the same concentration (2.78%). After 12 laundering cycles, the phosphorus content on the fabric treated with FR/ DMDHEU was 69% higher than that treated with FR/M-F. The data demonstrate that DMDHEU is not only much more effective for binding FR to cotton than M-F, and the bonding between FR and cotton formed by DMDHEU is also more durable to multiple home laundering than that formed by M-F.

The LOI and vertical flammability of the cotton fabric treated with 6% DMDHEU and FR at different concentrations and cured at 165°C for 2.5 min is presented in Tables 2 and 3, respectively. After one laundering cycle, the LOI of the fabric treated with FR/M-F is significantly higher than that treated with FR/DMDHEU. After 12 laundering cycles, the LOI of the fabric treated with FR/M-F was still higher than that treated

Table 2. The LOI of the cotton fabric treated with 6% crosslinking agents and FR at different concentrations, cured at 165°C for 2.5 min, and subjected to 1 and 12 home laundering cycles.

FR (%)	Crosslinker (%)	LOI (%)	
		1 HLTD	12 HLTD
25	DMDHEU 6	28.4	28.1
30	DMDHEU 6	29.5	29.2
35	DMDHEU 6	29.2	29.0
40	DMDHEU 6	29.4	29.2
45	DMDHEU 6	29.5	29.2
25	M-F 6	30.9	29.3
30	M-F 6	31.3	29.8
35	M-F 6	31.4	29.9
40	M-F 6	31.6	30.0
45	M-F 6	31.8	30.3

Table 3. The vertical flammability of the cotton fabric treated with 6% crosslinking agents and FR at different concentrations, cured at 165°C for 2.5 min, and subjected to 1 and 12 home laundering cycles.

FR (%)	Crosslinker (%)	Char length (mm)	
		1 HLTD	12 HLTD
25	DMDHEU 6	96	148
30	DMDHEU 6	97	109
35	DMDHEU 6	91	113
40	DMDHEU 6	94	109
45	DMDHEU 6	111	119
25	M-F 6	90	110
30	M-F 6	85	109
35	M-F 6	105	111
40	M-F 6	79	99
45	M-F 6	104	114

with FR/DMDHEU in spite of the fact that the phosphorus concentration on the cotton fabric treated FR/DMDHEU was approximately 70% higher than that treated with FR/M-F at the FR concentration range of 30–45% (Table 2).

The cotton fabric was treated with FR and a crosslinker (DMDHEU or M-F) at a 3:1 (w/w) ratio, and the FR concentration ranged from 4 to 40%. The treated fabric was cured at 165°C for 2.5 min. The LOI and vertical flammability of the cotton thus treated before and after 1 and 12 laundering cycles are presented in Table 4. The fabric treated with FR/M-F demonstrated better flame retarding performance at almost all cases in Table 4.

In summary, both DMDHEU and M-F function as the binders for FR and also as nitrogen provider to enhance the flame retarding performance of the treated cotton fabric. DMDHEU is a more effective crosslinker between FR and cotton, and the bonding formed by DMDHEU is also more durable to home laundering. When the concentrations of FR and the crosslinker reaches certain levels, however, the effect of phosphorus–nitrogen synergism becomes the predominant factor in determining the flammability of the treated cotton fabric even after multiple laundering cycles. The positive effect of M-Fs providing a higher level of phosphorus–nitrogen synergism exceeds the negative effect of M-Fs lower efficiency for bonding FR to cotton and its low laundering durability. Consequently, the cotton fabric treated with FR/M-F delivers superb flame retarding performance. In addition, the higher strength retention of the cotton fabric treated with FR/M-F is

Table 4. The flammability of the cotton fabric treated with FR/crosslinker (3:1, w/w) at with different concentrations and cured at 165°C for 2.5 min.

FR (%)	Crosslinker (%)	LOI (%)			Char Length (mm)		
		Before Wash	1 HLTD	12 HLTD	Before Wash	1 HLTD	12 HLTD
4	DMDHEU 1.3	22.5	20.0	19.7	>300	>300	>300
8	DMDHEU 2.7	23.6	21.5	21.4	>300	>300	>300
16	DMDHEU 5.3	28.3	27.1	25.0	98	107	>300
32	DMDHEU 10.7	32.5	30.6	30.5	92	95	104
40	DMDHEU 13.3	34.5	32.9	31.7	77	81	98
4	M-F 1.3	23.0	20.3	19.1	>300	>300	>300
8	M-F 2.7	26.2	23.5	22.3	>300	>300	>300
16	M-F 5.3	29.6	28.3	26.9	93	98	124
32	M-F 10.7	34.5	33.6	33.4	79	86	89
40	M-F 13.3	35.8	34.3	34.6	78	87	89

another advantage. M-F resin contains much higher levels of formalde-hyde than DMDHEU, which must be considered as a major disadvantage for the FR/M-F system.

CONCLUSION

DMDHEU and M-F both function as the binders for the hydroxy-functional organophosphorus flame retarding agent. DMDHEU is more effective for crosslinking cotton than M-F, thus cause higher fabric wrinkle resistance and higher fabric strength loss. DMDHEU is also more reactive for bonding FR to cotton than M-F, and the FR bound to cotton by DMDHEU is more durable to home laundering than that by M-F. Both DMDHEU and M-F also function as nitrogen providers for the flame-retardant system, thus enhancing its flame retarding performance. M-F is significantly better nitrogen provider than DMDHEU for the flame-retarding system. The cotton fabric treated with FR/M-F has significantly higher initial flame retarding properties than that treated with FR/DMDHEU. When the concentrations of the flame retarding organopho-sphorus compound and the crosslinker reach certain levels, the cotton fabric treated with FR/M-F maintain a higher level of flame retarding properties than that treated with FR/DMDHEU even after 12 home laundering cycles in spite of the fact that the phosphorus retention after multiple laundering cycles on the fabric treated with FR/DMDHEU is significantly higher than that treated with FR/M-F.

ACKNOWLEDGMENTS

REFERENCE

1. Weil, E.D. (1994). Phosphorus Flame Retardants, In: Kroschwitz, J.I. (ed.), *Kirk Othmer Encyclopedia of Chemical Technology*, Vol. 10, **4th edn**, pp. 976–998, John Wiley & Sons, Inc., New York.
2. Weil, E.D. (1992). Phosphorus-based Flame Retardants, In: Engel R. (ed.), *Handbook of Organophosphorus Chemistry*, pp. 683–738, Marcel Dekker, New York.
3. Horrocks, A.R. (1986). Flame-retardant Finishing of Textiles, *Rev. Prog. Coloration*, **16**(3): 62–66.

4. Stowell, J.K., Weil, E.D., Coble, W.L. and Yang, C.Q. (2002). US Patent 6,365,070 B1, Apr. 2, 2002.

5. Yang, C.Q. and Wu, W. (2003). Combination of a Hydroxy-functional Organophosphorus Oligomer and a Multifunctional Carboxylic Acids As a Flame Retardant Finishing System for Cotton: Part I. The Chemical Reaction, *Fire and Materials*, **27**(5): 223–237.

6. Yang, C.Q. and Wu, W. (2003). Combination of a Hydroxy-functional Organophosphorus Oligomer and a Multifunctional Carboxylic Acids As a Flame Retardant Finishing System for Cotton: Part II. Formation of Calcium Salt During Laundering, *Fire and Materials*, **27**(5): 239–251.

7. Weil, E.D. (1973). US Patent 3,746,572, July 17, 1973.

8. Chan, L.L. and Lau, P.W.K. (1994). Urea-Formaldehyde and Melamine-Formaldehyde Resins, in *Wet-Strength Resins and Their Application*, pp. 1–10, Tappi Press, Georgia, Atlanta.

9. Lewin, M. and Sello, S.B. (1983). Flame Retardance of Fabrics, in Chemical Processing of Fibers and Fabrics, Functional Finishes, in *Handbook of Fiber Science and Technology*, Vol. 2, pp. 47–327, Part A, (eds). Marcel Decker, New York.

10. Wu, W. and Yang, C.Q. (2003). Correlation Between Limiting Oxygen Index and Phosphorus/Nitrogen Content of the Cotton Fabric Treated with a Hydroxy-functional Organophosphorus Flame Retardant Finishing Agent and DMDHEU, *J. Apple. Polyp. Sci.*, **90**(7): 1885–1890.

11. Wu, W. and Yang, C.Q. (2003). Correlation Between Limiting Oxygen Index and Phosphorus Content of the Cotton Fabric Treated with a Hydroxy-functional Organophosphorus Flame Retardant Finishing Agent and Melamine-formaldehyde, *J. Fire Sci.*, in press.

12. Stevens, M.P. (1990). Phenol-, Urea-, and Melamine-formaldehyde Polymers, in *Polymer Chemistry*, **2nd edn**, pp. 483–484, Oxford University Press, New York.

13. Kang, I.S., Yang, C.Q. and Weir, W. (1998). Mechanical Strength of Durable Finished Cotton Fabric, *Textile Res. J.*, **68**(11): 865–870.

BIOGRAPHIES

Weidong Wu

Weidong Wu received his MS degree in textile chemistry from China Textile University, Shanghai, China in 1993, and is currently a PhD student at the University of Georgia.

Charles Q. Yang

Charles Q. Yang received his PhD degree in analytical chemistry from Kansas State University in 1987, and is currently a professor at the University of Georgia.

Exhibit C

ELSEVIER

Comparison of different reactive organophosphorus flame retardant agents for cotton: Part I. The bonding of the flame retardant agents to cotton

Weidong Wu[1], Charles Q. Yang*

Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, GA 30602, USA

Abstract

N-Methylol dimethylphosphonopropionamide (MDPA), known as "Pyrovatex CP" and "Pyrovatex CP New" commercially, has been one of the most commonly used durable flame retardant agents for cotton for many years. In our previous research, we developed a flame retardant finishing system for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO) in combination with a bonding agent such as trimethylolmelamine (TMM) and dimethyloldihydroxyethyleneurea (DMDHEU). In this research, we investigated the bonding of these two flame retardant finishing agents to cotton. We found that the majority of MDPA is bound to cotton by its *N*-methylol group and that the use of TMM as a co-reactant modestly increases the fixation of MDPA onto cotton. For HFPO, however, the use of a bonding agent is necessary to form a covalent linkage between HFPO and cotton. Both the fixation of HFPO on cotton and its laundering durability are influenced by the effectiveness and concentration of the bonding agent. The commercial product of HFPO contains approximately 33% more phosphorus than that of MDPA and the percent fixation of HFPO on cotton is also moderately higher than that of MDPA. The bonding between MDPA and cotton is significantly more resistant to hydrolysis during multiple launderings than that between HFPO and cotton. The selection of catalyst also plays a significant role in influencing the bonding of the flame retardant agents to cotton.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Cotton; Cellulose; Crosslinking; Flame retardant finishing; Organophosphorus chemical; Textile fibers

1. Introduction

Cotton, the most commonly used textile fiber, is also a highly combustible fiber. Flame retardant finishing of cotton fabrics and garments becomes necessary to improve human safety under many circumstances [1,2]. Most of the efforts in the area of textile flame retardant finishing have focused on reducing the flammability of cotton [3—9]. Various commercial versions of *N*-methylol dimethylphosphonopropionamide (MDPA)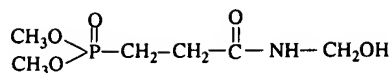 under the trade name of "Pyrovatex CP" and "Pyrovatex CP New" have been one of the most successful durable flame retardant agents for cotton since its introduction in 1968 [7—9]. The structure of MDPA is shown in Scheme 1. It was reported in the literature that MDPA was covalently bound to cellulose by the reaction between its *N*-methylol group and trimethylolmelamine (TMM) used as a co-reactant in the finishing system [10,11]. MDPA functions as a condensed-phase flame retardant agent to promote char formation [12].

In our previous research, we developed a flame retardant finishing system for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO) shown in Scheme 2 [13—18]. TMM and dimethyloldihydroxyethyleneurea (DMDHEU) were used as the bonding agents in the finishing system to form a covalent linkage between HFPO and cotton. HFPO, like MDPA, is also a condensed-phase flame retardant agent,

---

* Corresponding author. Tel.: +1 7065424912; fax: +1 7065424890.
  E-mail address: cyang@fcs.uga.edu (C.Q. Yang).
[1] Present address: Burlington WorldWide, 797 Main Street, Hurt, VA 24563, USA.

$$CH_3O \diagdown \underset{\underset{CH_3O \diagup}{}}{\overset{\overset{O}{\parallel}}{P}} - CH_2 - CH_2 - \overset{\overset{O}{\parallel}}{C} - NH - CH_2OH$$

Scheme 1. Structure of MDPA.

whereas TMM or DMDHEU functions as a nitrogen provider to enhance the performance of HFPO due to nitrogen—phosphorus synergism. The data will be discussed in a future paper. We studied the use of HFPO and DMDHEU to treat 100% cotton fleece and found that the HFPO/DMDHEU system has the potential to become a practical flame retardant finishing system for cotton raised surface fabrics [19].

The objective of this research was to investigate the bonding of the two reactive organophosphorus flame retardant agents to cotton and to compare the laundering durability of those flame retardant finishing agents after they are bound to cotton fabric. We also evaluated the effects of different catalysts on the bonding of these two flame retardant finishing agents to cotton.
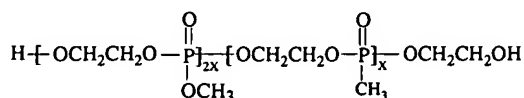
2. Experimental

2.1. Materials

The fabric used was a 3/1 twill weave 100% cotton fabric weighing 242 g/m^2. MDPA with the commercial name of "Pyrovatex CP New" (CA Registry No. 20120-33-6) was supplied by Ciba Specialty Chemicals, High Point, North Carolina. HFPO with the commercial name of "Fyroltex HP$^{\circledR}$" (also known as "Fyrol 51", CA Registry No. 70715-06-9) was supplied by Akzo Nobel Functional Chemicals, Dobbs Ferry, New York. DMDHEU with the commercial name of "Freerez 900" and TMM with the commercial name of "Aerotex M-3" were supplied by Noveon, Cleveland, Ohio. The NH_4Cl-based catalyst with the commercial name of "Catalyst RD" was supplied by Eastern Color & Chemical, Greenville, South Carolina. Phosphoric acid was a reagent grade chemical supplied by Aldrich Chemical, Milwaukee, Wisconsin. The $MgCl_2$-based "activated" catalyst with the commercial name of "Catalyst 531" was supplied by Omnova Solutions, Chester, South Carolina.

2.2. Fabric treatment and home laundering procedures

The fabric was first immersed in a finish solution containing a flame retardant agent, TMM or (DMDHEU + TMM), and a catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90 °C for 3 min, and finally cured in a Mathis curing oven at 165 °C for 2.5 min. The weight of H_3PO_4 (the catalyst for MDPA) was 2% of an MDPA finish

$$H \overline{\left(OCH_2CH_2O - \underset{\underset{OCH_3}{|}}{\overset{\overset{O}{\parallel}}{P}} \right)}_{2x} \overline{\left(OCH_2CH_2O - \underset{\underset{CH_3}{|}}{\overset{\overset{O}{\parallel}}{P}} \right)}_{x} OCH_2CH_2OH$$

Scheme 2. Structure of HFPO.

bath. The weight of "Catalyst RD" (the catalyst for HFPO) was 2% of that of TMM or (DMDHEU + TMM). Concentrations (w/w, %) of MDPA and HFPO were calculated based on the weight of the commercial products. The concentrations (w/w, %) of TMM and DMDHEU were calculated based on the weight of the active reagent since the commercial products are less than 100% active. All the concentrations presented are based on weight of the bath (wob). The wet pick-up of the cotton fabric was approximately 80 ± 3%. After curing, the treated cotton fabric was subjected to different numbers of home laundering cycles with the use of a reference detergent ("AATCC Standard Detergent 1993"). The home laundering procedure was done according to AATCC Test Method 124 ("Appearance of Fabrics after Repeated Home Laundering"). The water temperature for laundering was approximately 46 °C.

2.3. Fabric performance evaluation

The limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM Method D2863.

2.4. Determination of phosphorus (P) concentration on the treated cotton fabric

Approximately 2 g of treated cotton fabric taken from three different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Two milliliters of concentrated H_2SO_4 were added to 0.1 g of the cotton powder. Ten milliliters of 30% H_2O_2 were added drop-wise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250 °C to digest the powder and to evaporate the water until dense SO_3 vapor was produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the P content. The *percent P fixation* on a treated fabric sample was calculated using the formula $(P_{al}/P_{bl}) \times 100\%$, where P_{al} is the P content (%) on the fabric after one laundering cycle and P_{bl} is the P content (%) on the fabric before laundering. The *percent P retention* after multiple home laundering cycles was calculated using the formula $(P_{aml}/P_{bl}) \times 100\%$, where P_{aml} is the P content (%) on the fabric after specified laundering cycles.

2.5. Carbon, hydrogen, and nitrogen (C, H and N) analysis

The concentrations of C, H and N of the commercial products of MDPA and HFPO were analyzed with a PE 240C C/H/N analyzer. Approximately 2 mg of a sample were first combusted, and the combustion products were separated by chemical chromatography and measured quantitatively by a thermal conductivity detector to determine the C, H, and N concentrations.

Table 1
The P, N, C and H contents (%, w/w) of HFPO and MDPA[a]

Product	P (%)			N (%)		C (%)		H (%)	
	Theoretical	Measured	Ratio (measured/theoretical)	Theoretical	Measured	Theoretical	Measured	Theoretical	Measured
HFPO	20.22	19.56	96.7	0	0	28.69	29.92	5.87	6.06
MDPA	14.69	14.70	100.1	6.64	6.77	34.12	33.35	6.64	6.90

[a] The theoretical values were calculated based on the molecular formulas shown in Scheme 2 assuming $x = 1$. The theoretical values of P, C and H contents were 21.68, 27.97 and 5.60%, respectively, when $x = 2$.

3. Results and discussion

3.1. The composition of MDPA and HFPO

The percent content of P in MDPA and HFPO was determined using ICP/AES whereas their C, H and N contents were measured by a C/H/N analyzer. Both the theoretical and measured values of P, C, H and N are presented in Table 1. The measured P concentration of HFPO is 19.56% whereas the theoretical value based on the formula shown in Scheme 2 is 20.22% (Table 1). Thus, the purity of HFPO is 96.7% assuming that all the phosphorus in the product come from the active ingredient shown in Scheme 2. The measured values of both C and H contents of HFPO are slightly higher than their corresponding theoretical values probably due to the presence of residual reactants and reaction intermediates in the commercial product. Based on the measured and theoretical values of the phosphorus content of MDPA presented in Table 1, the purity of MDPA is nearly 100%. The data presented in Table 1 also show that the P content of the commercial product of HFPO is approximately 33% higher than that of MDPA.

3.2. The bonding of MDPA to cotton

The cotton fabric was first treated with the MDPA solutions at concentrations ranging from 8 to 48% in combination with H_3PO_4 as the catalyst, cured at 165 °C for 2.5 min, and finally subjected to one laundering cycle to remove the MDPA not

fixed to cotton. The P content and the percent P fixation on the cotton fabric thus treated are presented as a function of the MDPA concentration (wob%) in Figs. 1 and 2, respectively. The fabric treated with 8% MDPA has 1.07% P before laundering, and the P concentration decreases to 0.56% after one laundering cycle (Fig. 1), which represents 51% fixation of P on the fabric (Fig. 2). The percent P fixation appears to be unchanged as the MDPA concentration is increased from 8 to 48% (Fig. 2).

The literature reported that MDPA was bound to cotton cellulose by the reactions of TMM with both MDPA and cellulose as shown in Scheme 3 [9,11]. The data presented here, however, clearly indicate that MDPA is able to react directly with cellulose through its N-methylol group (Scheme 4). The concentration of the MDPA bound to cotton increases almost linearly as the concentration of the MDPA applied to the fabric is increased (Fig. 1). However, the percent P fixation remains practically unchanged (50—52%) as the MDPA concentration is increased from 8 to 48% (Fig. 2). Thus, the data presented in Fig. 2 show that the percent fixation of MDPA on cotton is independent of the concentration of the MDPA solutions used to treat the fabrics (Fig. 2).

The cotton fabric is treated with 45% MDPA and cured at 165 °C for 2.5 min, then subjected to 50 home laundering cycles. The percent P retention of the fabric thus treated is plotted against the number of home laundering cycles in Fig. 3. The P retention of the treated fabric is 51% after one laundering cycle, and it is still 49% after 50 laundering cycles (Fig. 3). The data presented here demonstrate that the bonding between MDPA and cotton ($-C[=O]-NH-CH_2-O-CH_2-$, shown in
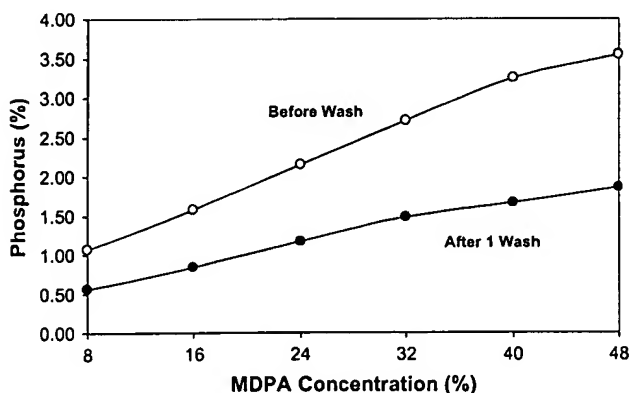

Fig. 1. Percent P content of the cotton fabric treated with MDPA at different concentrations and cured at 165 °C for 2.5 min as a function of MDPA concentration (before and after 1 home laundering cycle).
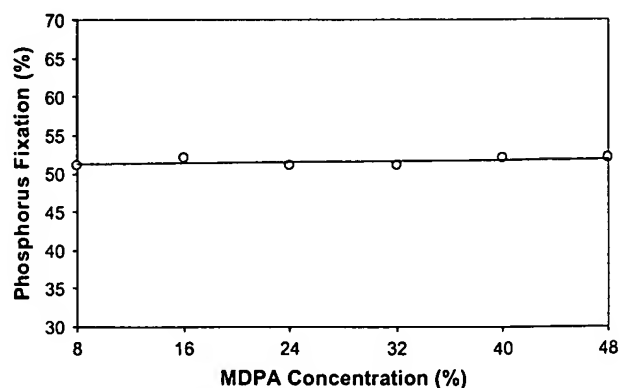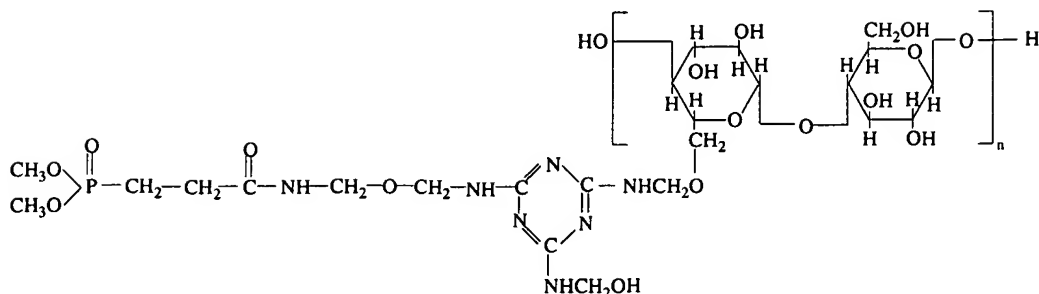

Fig. 2. Percent P fixation of the cotton fabric treated with MDPA, cured at 165 °C for 2.5 min as a function of MDPA concentration.

Scheme 3. The bonding of MDPA to cotton via TMM.

Scheme 4) is highly resistant to hydrolysis during multiple home launderings.

Shown in Fig. 4 is the *P* retention of the cotton fabric treated with 45% MDPA in combination with TMM at different concentrations and cured at 165 °C for 2.5 min (after 1 and 50 laundering cycles) as a function of the TMM concentration. One observes that the percent *P* fixation of the treated fabric steadily increases from 50 to 63% (a 26% increase) as the TMM concentration is increased from 0 to 8%, and *P* retention increases from 48 to 59% (a 23% increase) after 50 laundering cycles in the same TMM concentration range (Fig. 4). A portion of the cellulosic hydroxyl groups in a cotton fiber, which is probably not accessible by the MDPA molecule because of its relatively large size, is able to bind cellulose through reactions with the *N*-methylol groups of TMM which also react with cellulose. Consequently, more MDPA is able to bind to cotton through the TMM bridges, as shown in Scheme 3, and the percent *P* fixation increases by 26% when 8% TMM is added to the formula (Fig. 4). It is evident that the majority of MDPA is bound to cotton via its methylol group and the bonding is highly resistant to hydrolysis. The use of TMM as a co-reactant modestly increases the percent fixation of MDPA.

3.3. The bonding of HFPO to cotton

Because HFPO does not have any reactive functional group to form covalent bonding with cotton, it is necessary to use a bonding agent, such as TMM or DMDHEU, to bind it to cotton [13,16]. The cotton fabric is treated with 32% HFPO in combination with TMM or with (DMDHEU + TMM) (1:1, w/w), then cured at 165 °C for 2.5 min. The percent *P* fixation and the percent *P* retention after 50 home launderings of the

treated fabric are presented as functions of the nominal total binder concentration of the solutions in Figs. 5 and 6, respectively. The percent *P* fixation of the fabric treated with HFPO without a bonding agent is insignificant. When 2% (DMDHEU + TMM) or 2% TMM are present in the finish solutions, the *P* fixation becomes 40 and 32%, respectively (Fig. 5). The percent *P* fixation of the treated fabric increases as the concentration of the bonding agents is increased (Fig. 5). The data presented in Fig. 5 also indicate that the percent *P* fixation of the fabric treated with (DMDHEU + TMM) is higher than that treated with TMM. The higher *P* fixation for the fabric treated using (DMDHEU + TMM) as the bonding agents is due to the higher reactivity of DMDHEU to form a "bridge" between HFPO and cellulose than TMM as discussed in our previous research [13,16]. Because a bonding agent or mixtures of bonding agents are necessary for HFPO to be bound to cotton, the reactivity and concentration of the bonding agent play critical roles in determining percent fixation of HFPO to cotton.

One also observes that the difference in percent *P* fixation becomes smaller as the binder concentration increases (Fig. 5). When 8% (DMDHEU + TMM) and 8% TMM were used, the percent *P* fixation is 71% and 69%, respectively (Fig. 5). After 50 launderings, the *P* retention of the fabric treated using 8% TMM becomes 41%, which is higher than that treated using (DMDHEU + TMM) (38%, Fig. 6). The data presented here indicate that the fabric treated with HFPO/TMM shows higher resistance to hydrolysis during the 50 laundering cycles than that treated with HFPO/(TMM + DMDHEU) when the TMM concentration is increased to 8% (Fig. 6). In our previous research, we discovered that TMM at certain HFPO/TMM ratios was able to react with HFPO to form a crosslinked polymer network on the fabric as shown in Scheme 5. The
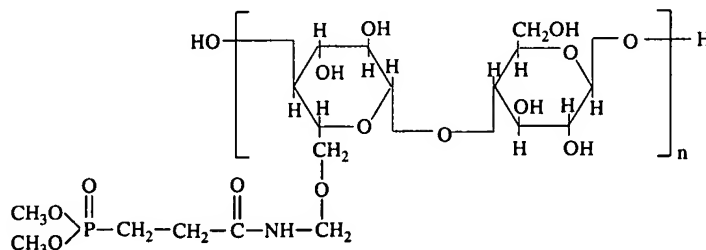
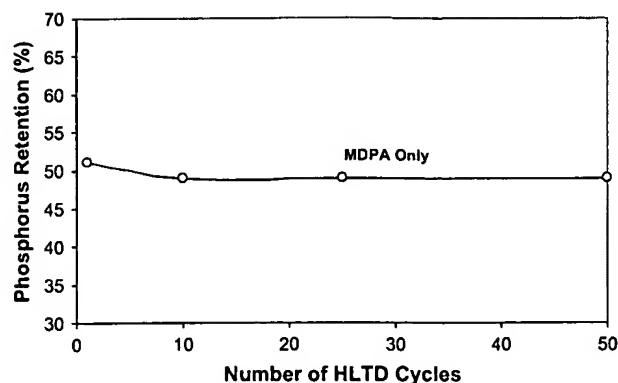Scheme 4. The direct bonding of MDPA to cotton.

Fig. 3. P retention of the cotton fabric treated with 45% MDPA and cured at 165 °C for 2.5 min as a function of the number of home laundering cycles.

formation of the HFPO/TMM crosslinked polymeric network improves the laundering durability of the HFPO on cotton [17].

3.4. The percent fixation and laundering durability of MDPA and HFPO on cotton

The cotton fabric is treated with the combination of 45% MDPA and 8% TMM, the combination of 32% HFPO and 8% (DMDHEU + TMM), and the combination of 32% HFPO and 8% TMM. The treated fabric is cured at 165 °C for 2.5 min and subjected to different numbers of home laundering cycles. The P concentration of the cotton fabric thus treated and subjected to different home laundering cycles is presented in Table 2. The percent P retention of the cotton fabric is shown against the number of laundering cycles in Fig. 7. The cotton fabric treated with MDPA/TMM has 2.29% P after one laundering cycle, which represents 65% P fixation on the fabric. The P concentrations of the fabric treated with HFPO/ TMM and HFPO/(DMDHEU + TMM) are 2.39% and 2.46% after one laundering cycle, which represent 69 and 71% P fixation, respectively (Fig. 7). The fabric treated with HFPO shows modestly higher percent P fixation than that treated with MDPA, but significantly lower percent P retention

Fig. 5. Percent P fixation of the cotton fabric treated with 32% HFPO in combination of TMM or (DMDHEU + TMM) and cured at 165 °C for 2.5 min as a function of the total binder concentration.

when the numbers of home laundering cycle increase to 25 and 50 (Fig. 7).

MDPA is bound to cotton cellulose by its N-methylol group's reactions either directly with cotton cellulose or with the added TMM whereas HFPO is bound to cotton only by the "bridges" between HFPO and cotton formed by DMDHEU or TMM. The relatively smaller size of TMM and DMDHEU compared with that of MDPA probably makes the methylol groups in their molecules to easily access the cellulosic hydroxyl of cotton.

In order to examine the effects of different N-methylol concentrations on the percent P fixation, we conducted the following experiment. The cotton fabric is treated with the combination of 45% MDPA and TMM at concentrations ranging from 0 to 8% and also with the combination of 32% HFPO and TMM at the same concentration range, then cured at 165 °C for 2.5 min. The cotton fabric thus treated contains approximately the same P ($\sim$3.5%) content before laundering. The percent P fixation of the fabric treated with the two flame retardant systems is presented as a function of the N-methylol/ phosphorus mole ratio in the finish systems in Fig. 8. The N-methylol/phosphorus mole ratio of MDPA without TMM is 1.0, and the cotton fabric treated with 45% MDPA has

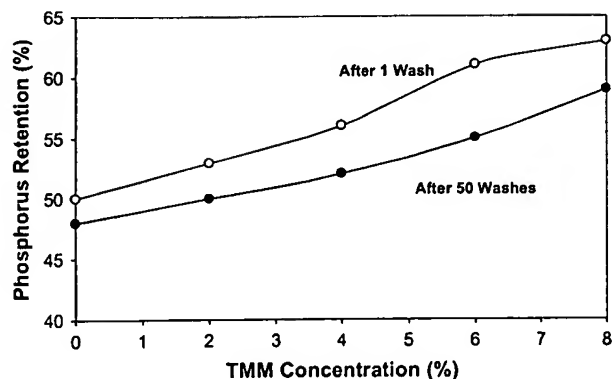Fig. 4. P retention of the cotton fabric treated with 45% MDPA in combination of TMM with different concentrations and cured at 165 °C for 2.5 min as a function of TMM concentration (after 1 and 50 home laundering cycles).
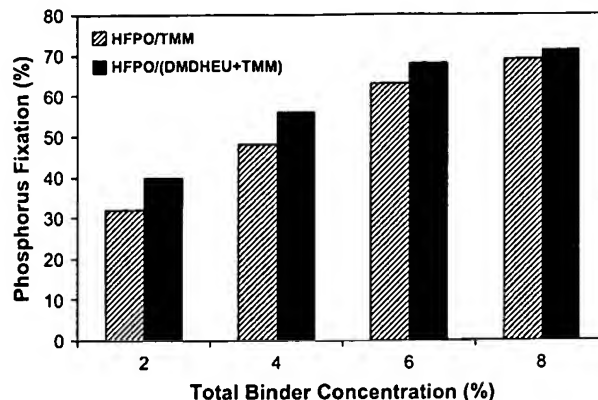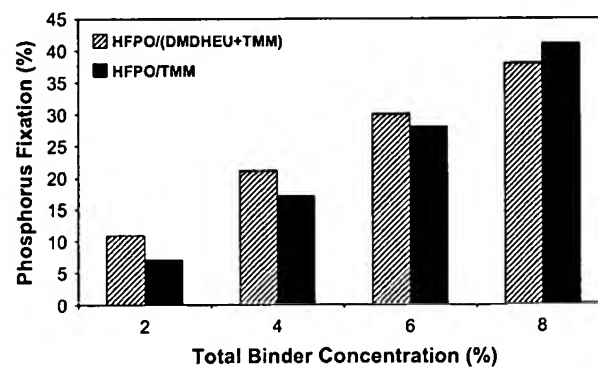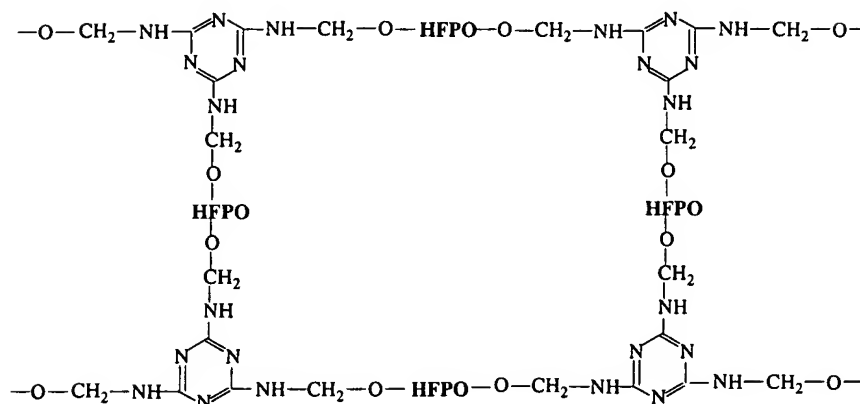

Fig. 6. P retention of the cotton fabric treated with 32% HFPO in combination of TMM or (DMDHEU + TMM) and cured at 165 °C for 2.5 min after 50 home laundering cycles as a function of the total binder concentration.

Scheme 5. The crosslinked polymeric network of HFPO/TMM.

51% P fixation. The fabric treated with 32% HFPO and 4% TMM (N-methylol/phosphorus mole ratio: 0.27 assuming that both HFPO and TMM have 100% active ingredient) has 49% P fixation, which is very close to that of the fabric treated with MDPA without TMM. The cotton fabric treated with the combination of 45% MDPA and 8% TMM (N-methylol/phosphorus ratio: 1.52) has the percent P fixation of 63%. The fabric treated with the combination of 32% HFPO and 6% TMM (N-methylol/phosphorus ratio: 0.40) achieves the same percent P fixation of 63% (Fig. 8). The N-methylol/phosphorus mole ratio increases to 1.0 for the HFPO/TMM system when the TMM concentration is increased to 15.3%. The percent P fixation of the fabric thus treated reaches 78%, which is 53% higher than that of the fabric treated with MDPA at the same N-methylol/phosphorus mole ratio (Fig. 8). The data presented in Fig. 8 clearly indicate that the number of moles of phosphorus initially bound to cotton is significantly higher for the HFPO system than for MDPA system when the equal moles of N-methylol (based on the same number of moles of P) are present in the systems. It also means that the number of moles of N-methylol required to bond 1 mol of phosphorus of HFPO to cotton is significantly lower than that required to bond 1 mol of MDPA to cotton. This is because that ≥ 1 mol N-methylol is need to bond 1 mol of phosphorus to cotton for MDPA (Schemes 3 and 4), whereas only 0.67 mol N-methylol is needed to bond 1 mol P for the HFPO/TMM system.

Assuming $x = 1$ in the molecule of HFPO shown in Scheme 2, each HFPO molecule has three P atoms whereas each TMM

Table 2
The P concentration of the cotton fabric treated with the combination of 45% MDPA and 8% TMM, the combination of 32% HFPO and 8% TMM, and the combination of 32% HFPO and 8% (DMDHEU + TMM), and cured at 165 °C for 2.5 min

Flame retardant system	Phosphorus (%)				
	Before wash	After 1 wash	After 10 washes	After 25 washes	After 50 washes
HFPO/ (DMDHEU + TMM)	3.46	2.46	2.08	1.83	1.38
HFPO/TMM	3.46	2.39	2.10	1.73	1.42
MDPA/TMM	3.50	2.29	2.17	2.10	2.06

molecule also has three N-methylol groups. The HFPO/TMM mole ratio of the crosslinked polymeric network shown in Scheme 5 is 1.5:1.0, therefore the N-methylol/phosphorus mole ratio in the crosslinked network is 0.67:1.0. It means that each mole of phosphorus requires 0.67 mol of N-methylol to be bound to cotton via the crosslinked polymeric networks. The phosphorus/N-methylol mole ratio in an MDPA molecule is 1:1, therefore 1 mol of N-methylol is needed to bond 1 mol of P to cotton if all the MDPA are bound to cotton via the N-methylol group in its molecule. The required number of moles of N-methylol becomes even higher if TMM also participates in bonding MDPA to cotton as shown in Scheme 3.

The P content of the cotton fabric treated with the combination of 45% MDPA and 8% TMM after 50 laundering cycles is 2.06% (Table 2), which represents 59% of the P retention on fabric and a 10% decrease in P compared to that after one laundering cycle. Meanwhile, the P content of the fabric treated with the combination of 32% HFPO and 8% TMM was 1.42% after 50 laundering cycles (Table 2), which represents 41% retention of the phosphorus applied to the fabric and a 41% decrease in P concentration compared to that after one laundering cycle (Fig. 7). The data presented here unmistakably demonstrate that the resistance of MDPA on cotton to the hydrolysis during multiple launderings is significantly
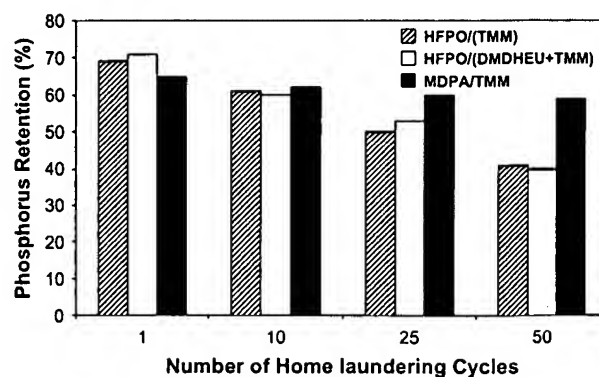

Fig. 7. P retention of the cotton fabric treated with 45% MDPA or 32% HFPO in combination of 8% bonding agents and cured at 165 °C for 2.5 min as a function of the number of home laundering cycles.
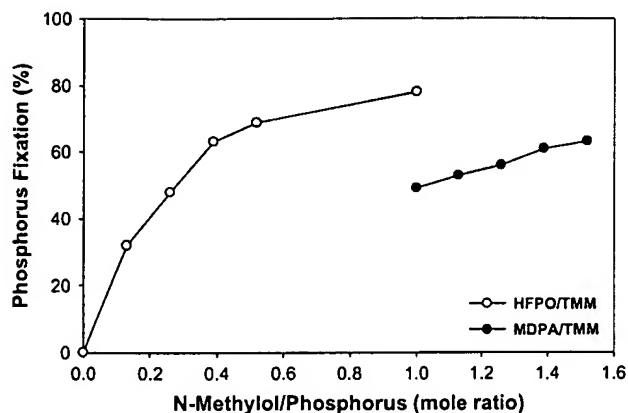
Fig. 8. Percent P fixation of the cotton fabric treated with the combination of 45% MDPA and TMM at different concentrations, and with the combination of 32% HFPO and TMM at different concentrations, cured at 165 °C for 2.5 min as a function of mole ratio of N-methylol/phosphorus.

higher than that of HFPO. There are possibly two explanations for the different hydrolysis resistance. First, the bonding of DMDHEU/TMM with HFPO and cellulose is less resistant to the hydrolysis during laundering than that between MDPA and cellulose. Secondly, the hydrolysis of any two methylol groups of TMM results in loss of one HFPO molecule (three phosphorus atoms) based on the structure shown in Scheme 5. Therefore, 1.5 mol of P is lost for the hydrolysis of 1 mol of the $\geq N-CH_2-O-CH_2-$ group in the HFPO/TMM cross-linked network. For MDPA, however, the hydrolysis of 1 mol $-NH-CH_2-O-CH_2-$ results in loss of 1 mol of P since the majority of P is bound to cotton by the methylol group of MDPA.

The P retention of the treated cotton fabric after 50 home laundering is presented as a function of the N-methylol/phosphorus mole ratio in Fig. 9. The cotton fabric treated with 45% MDPA without TMM (N-methylol/phosphorus mole ratio: 1.0) has 49% P retention after 50 laundering cycles whereas the fabric treated with 45% MDPA and 8% TMM (N-methylol/
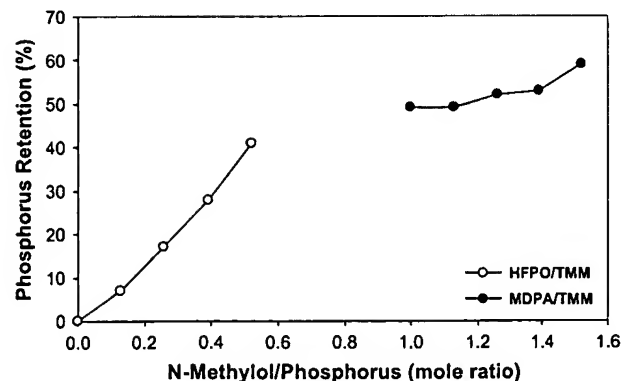

Fig. 9. P retention of the cotton fabric treated with the combination of 45% MDPA and TMM at different concentrations, and with the combination of 32% HFPO and TMM at different concentrations, cured at 165 °C for 2.5 min as a function of mole ratio of N-methylol/phosphorus (after 50 home laundering cycles).

phosphorus ratio: 1.52) has 59% P retention (Fig. 9). The cotton fabric treated with 32% HFPO and 6% TMM (N-methylol/phosphorus ratio: 0.40) has 28% P retention after 50 laundering cycles. As the TMM concentration is increased to 8% and the N-methylol/phosphorus mole ratio is increased to 0.54 accordingly, the P retention of the treated fabric increases to 41% after 50 laundering cycles (Fig. 9). The curves in Fig. 9 demonstrate the dependency of the P retention after 50 laundering cycles on the N-methylol/phosphorus mole ratio of the flame retardant finish systems. One also observes in Fig. 9 that the HFPO/TMM curve has a much steeper slope than the MDPA curve. Because HFPO does not have a reactive functional group to react with cotton, therefore it depends entirely on TMM or DMDHEU to form covalent bonding between cotton and HFPO. For MDPA, however, its bonding to cotton is mainly due to the reaction between its methylol group and cotton, and addition of TMM only plays a minor role in the bonding of MDPA as discussed previously. Consequently, the resistance to hydrolysis during laundering of HFPO depends much more on the quantity of TMM than that of MDPA.

3.5. The catalysts for the bonding MDPA and HFPO to cotton

We studied the effects of different catalysts on the bonding between the two flame retardant systems and cotton. The cotton fabric was treated with the combination of 45% MDPA and 6% TMM and also with the combination of 32% HFPO and 6% TMM or 6% (DMDHEU + TMM). Three catalyst systems based on H_3PO_4, NH_4Cl and $MgCl_2$ are used in the formulas. The percent P fixation and LOI (%) of the fabric thus treated after one laundering cycle are shown in Tables 3 and 4, respectively. When the three catalysts are used for the MDPA/TMM system, the formula containing H_3PO_4 as the catalyst provides the highest percent P fixation (61%) on

Table 3

The percent P fixation of the cotton fabric treated with the MDPA and HFPO systems using different catalysts and cured at 165 °C for 2.5 min

Catalyst type	Phosphorus fixation (%)		
	32% HFPO/6% TMM	32% HFPO/6% (DMDHEU + TMM)	45% MDPA/6% TMM
H_3PO_4	55	61	61
NH_4Cl	63	68	53
$MgCl_2$	56	62	51

Table 4

The LOI of the cotton fabric treated with the MDPA and HFPO systems using different catalysts and cured at 165 °C for 2.5 min (after 1 home laundering)

Catalyst type	LOI (%)		
	32% HFPO/6% TMM	32% HFPO/6% (DMDHEU + TMM)	45% MDPA/6% TMM
H_3PO_4	32.3	32.0	33.3
NH_4Cl	33.6	32.2	29.8
$MgCl_2$	32.4	32.0	29.5

the fabric, which is approximately 20% higher than that of the fabric treated with $MgCl_2$ as catalyst (Table 3). Consequently, the LOI of the fabric treated by MDPA with H_3PO_4 as the catalyst (33.3%) is significantly higher than that treated with NH_4Cl and $MgCl_2$ as the catalysts (29.8 and 29.5%, respectively, Table 4). The superior performance of the fabric treated with H_3PO_4 as catalyst demonstrates that H_3PO_4 is the optimum catalyst for MDPA.

When these three catalysts are applied to the two HFPO formulas, the cotton fabric treated using the NH_4Cl-based catalyst shows the highest percent P fixation (Table 3). The fabric treated with HFPO/(DMDHEU + TMM)/NH_4Cl has percent P fixation of 68%, which is significantly higher than that treated using the two other catalysts (H_3PO_4 and $MgCl_2$). The fabric treated with HFPO/TMM/NH_4Cl has the highest percent P fixation (63%) among the fabric samples treated with the three HFPO/TMM formulas (Table 3). The LOI of the fabric treated with HFPO/TMM/NH_4Cl (33.6%) is significantly higher than that treated using the other two catalysts (33.3 and 33.4%, Table 4). Thus, the data presented in Tables 3 and 4 indicate that the NH_4Cl-based catalyst is the most effective catalyst system for HFPO/TMM. The selection of a catalyst for the flame retardant finishing system apparently plays an important role in influencing the bonding of these flame retardant finishing systems to cotton.

4. Conclusions

MDPA can be bound to cotton cellulose by N-methylol group in its molecule. The percent fixation of MDPA on the cotton fabric is independent of its concentration applied to the fabric. The presence of TMM as a co-reactant modestly increases the amount of MDPA bound to cotton. For HFPO, a bonding agent such as TMM or DMDHEU is necessary for HFPO to be bound to cotton. The effectiveness and concentration of the bonding agent determine the percent fixation and the laundering durability of the HFPO bound to cotton.

The percent fixation of HFPO on cotton is moderately higher than that of MDPA. However, the MDPA bound to cotton has significantly higher resistance to hydrolysis during multiple home launderings than the HFPO. The higher laundering durability of MDPA on the cotton fabric is attributed to the higher content of N-methylol contained in the system.

H_3PO_4 is the optimum catalyst for the MDPA system whereas the NH_4Cl-based catalyst is the optimum catalyst for the HFPO system.

References

[1] Horrocks AR. Flame-retardant finishing of textiles. Rev Prog Color 1986;16:62.
[2] Horrocks AR. In: Heywood D, editor. Textile finishing. West Yorkshire, U.K: Society of Dyers and Colourists; 2003. 214 p.
[3] Tesoro CG, Sello BS, Willard JJ. Flame-retardant properties of phosphonate derivatives of cotton cellulose. Text Res J 1968;38:245.
[4] LeBlanc RB. Degradation of pyrovatex-treated fabric during storage. Text Res J 1989;59:307.
[5] Hebeish A, Waly A, Abou-Okeil AM. Flame retardant cotton. Fire Mater 1999;23:117.
[6] Lecoeur E, Vroman I, Bourbigot S, Lam TM, Delobel R. Flame retardant formulations for cotton. Polym Degrad Stab 2001;74:487.
[7] Weil ED. In: Grayson M, editor. Kirk Othmer encyclopedia of chemical technology. 4th ed. New York: Wiley; 1995. 976 p.
[8] Weil ED. In: Engel R, editor. Handbook of organophosphorus chemistry. New York: Marcel Dekker; 1992. 683 p.
[9] Aenishanslin R, Guth C, Hofmann P, Maeder A, Nachbur H. A new chemical approach to durable flame-retardant cotton fabrics. Text Res J 1969;39:375.
[10] Tesoro GC, Sello SB, Willard JJ. Nitrogen–phosphorus synergism in flame-retardant cellulose. Text Res J 1969;39:180.
[11] Horrocks AR. In: Heywood D, editor. Textile finishing. West Yorkshire, U.K: Society of Dyers and Colourists; 2003. 229 p.
[12] Egyed O, Simon J. Nitrogen–phosphprus synergism in flame-retardant cellulose. J Therm Anal 1979;16:321.
[13] Wu W, Yang CQ. Statistical analysis of the performance of the flame retardant finishing system consisting of a hydroxy-functional organophosphorus oligomer and the mixture of DMDHEU and melamine–formaldehyde resin. Polym Degrad Stab 2004;84:623.
[14] Yang H, Yang CQ. Durable flame-retardant finishing of the nylon/cotton blend fabric using a hydroxyl-functional organophosphorus oligomer. Polym Degrad Stab 2005;88:363.
[15] Yang CQ, Wu W, Yang H. Textile processing: state of art & future development. Cairo, Egypt: Textile Research Division, National Textile Center; 2005. 128 p.
[16] Wu W, Yang CQ. Comparison of DMDHEU and melamine–formaldehyde as the binding system for a hydroxy-functional organophosphorus flame retarding agent on cotton. J Fire Sci 2004;22:125.
[17] Yang CQ, Wu W. The combination of a hydroxy-functional organophosphorus oligomer and melamine–formaldehyde as a flame retarding system for cotton. Fire Mater 2005;29:109.
[18] Stowell JK, Yang CQ. A durable low-formaldehyde flame retardant finish for cotton fabrics. AATCC Rev 2003;3(2):7.
[19] Yang CQ, Qiu X. Flame retardant finishing of cotton fleece: part I. The use of a hydroxy-functional organophosphorus oligomer and DMDHEU. Fire Mater, in press.